

Examination of a coffee product enriched with calcium by the isoperibolic method

B. Schäffer · B. Keller · Z. Szakály ·
D. Lőrinczy

Received: 30 July 2011 / Accepted: 5 September 2011 / Published online: 18 September 2011
© Akadémiai Kiadó, Budapest, Hungary 2011

Abstract The main reason of osteoporosis, one of the most frequently occurring civilization disease nowadays, is the calcium-deficient and phosphorus-surplus nutrition, respectively. One of the possible preventions is to complete the foods with predominance of phosphorus with Ca at least till Ca:P ratio of 1:1. To complete foods with Ca today primarily organic Casalts (e.g. Ca-malate, -lactate, -citrate) are used, their absorption has clinically been approved. These Ca-enrichers are food additives and have E-numbers. The raw material of a Ca-enricher has been developed by us is the Ca-rich whey of fermented fresh cheese being indigenous in the Carpathian basin, and which is further enriched in Ca (first of all in Ca-malate) during the technology. This product being under EU-patentization, contains the main adjuvants (milk protein, lactose, oligosaccharide, micro elements) promoting the Ca-absorption and incorporation in bones. It is an additive-food, its bioavailability has clinically been proved. Its further advantage is that owing to its colloidchemical structure it can be instantized. In our experiments separately 20–20 mg from calcium-malate

(CaM), fresh cheese whey powder enriched in Ca (QC), its instant version (QC_i), instant coffee (DE), mixture of 50–50% instant coffee and instant fresh cheese whey powder enriched in Ca (DEQC_i) were measured into the bottom of a mixing batch vessel and 180 mg distilled water into the upper part of it (in the reference one 20 + 180 mg distilled water). Attaining the heat balance the two parts of the cell have been mixed and the isotherm solution curves have been plotted at 20°C. Our main results are: (i) There is no significant difference between the heat amounts liberated in CaM, QC and QC_i plus water solutions. The average value of enthalpies is –28 J/g. (ii) There are one maximum peak at CaM and two peaks at QC during solution. The CaM, and the first maximum peaks of QC are in the range of 700–800 s after mixing, and the second peak is within 2000–4000 s. The total solution at both samples is over 6000 s. (iii) At instant sample (QC_i) there is one maximum at 100 s and the solution is completed at about 700 s. (iv) The slope of DE and DEQC_i curves are the same.

Béla Schäffer during the preparation of the manuscript unexpectedly passed away.

B. Schäffer · B. Keller
Pécsi Milker Food Science Co. Ltd., Nyírfa u. 2/a, 7622 Pécs,
Hungary

Z. Szakály
Department of Marketing and Trade, Faculty of Economics,
Kaposvár University, Guba S. u. 40, 7400 Kaposvár, Hungary

D. Lőrinczy (✉)
Institute of Biophysics, Faculty of Medicine, University of Pécs,
Szigeti Str. 12, 7624 Pécs, Hungary
e-mail: denes.lorinczy@aok.pte.hu

Keywords Isoperibol calorimetry · Osteoporosis ·
Ca:P ratio · Instant coffee

Introduction

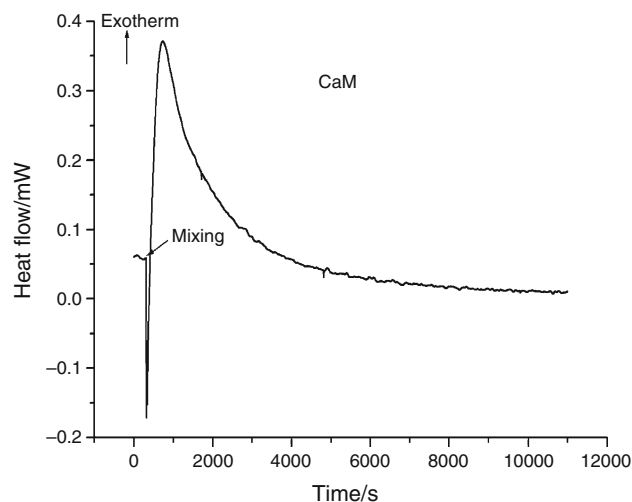
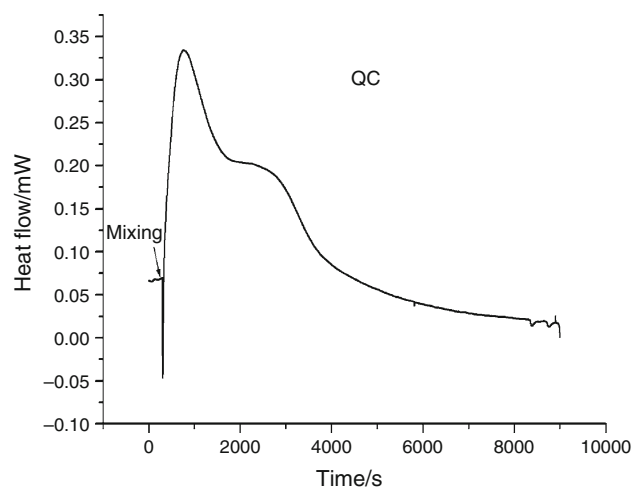
All over the world, but, first of all, in so called ‘civilized’ countries the osteoporosis, the ‘latent epidemic’ is still spreading. The situation is especially critical in countries, where the milk product consumption is low or decreasing e.g., in Hungary [1]. Besides, the low intake of calcium the primary cause of osteoporosis is the predominance of

Table 1 Physical, chemical and microbiological characteristics of Calcima® QC

Physical characteristics		
Appearance	Off-white, homogeneous flowing powder	
Solubility	Optionally changeable according to demand of use	
Odour/taste	Clean, remembering to whey powder	
Chemical characteristics		
Denomination	Dimension	Average value
Dry matter	%	95–98
Moisture	%	2–5
Lactose + oligosaccharide	%	27–37
Protein	%	5.3–8.8
Fat	%	≤1.0
Organic and inorganic salts within	%	52.0–62.0
Calcium (Ca)	%	10–13
Phosphorus (P)	%	0.4–0.6
Ca:P ratio		20:1
Magnesium (Mg)	%	0.1–0.3
Potassium (K)	%	0.8–1.4
Sodium (Na)	%	0.4–0.6
Manganese (Mn)	mg/100 g	0.2–0.5
Copper (Cu)	mg/100 g	0.1–0.3
Zinc (Zn)	mg/100 g	2–3
<i>Within Ca salts</i>		
Organic bond	%	92
Inorganic bond	%	8
Heavy metals		
As	mg/kg	<0.5
Hg	mg/kg	<0.01
Pb	mg/kg	<1.0
Cd	mg/kg	<0.5
Acidity	pH	5.2–5.6
Microbiological characteristics		
Salmonella	/25 g	0
<i>Staphylococcus aureus</i>	/g	<i>m</i> : <0.3, <i>M</i> : <10
<i>Escherichia coli</i>	/g	<i>m</i> : <0.3, <i>M</i> : <10
Enterobacteriaceae	/g	<i>m</i> : <0.3, <i>M</i> : <10
Moulds	/g	<10
Yeasts	/g	<10
Total plate count	/g	<10 ⁴

phosphorus in nutrition, i.e., bad Ca:P ratio of foodstuffs. Ca and P in ratio at least 1:1 got from the diet play also an important role in prevention and therapy of diseases like high blood pressure, colon diseases (e.g., colon cancer), kidney stone formation and diabetes [2].

The basic objective is therefore to increase dietary Ca-intake in a way that Ca:P ratio should be at least 1:1.

**Fig. 1** The isotherm solution curve of calcium-malate (CaM)**Fig. 2** The isotherm solution curve of fresh cheese whey powder enriched in Ca (QC)

However, the Hungarian example shows that due to nutritional customs this objective is very difficult to be attained. Examining the Ca- and P-intake of the Hungarian population in the period from 1985 to 2004 it can be stated that inspite of quantitative and qualitative change of foods consumed, the dietary Ca:P ratio remained the same [3]. The ratio in both years was 1:2.

One of the possibilities to improve the dietary Ca:P ratio is to enrich the foods which have surplus phosphorus or another ingredient (e.g., caffeine) promoting discharge of Ca from the body with Ca. For enrichment those food additives are suitable which contain Ca in a bioavailable form. Bioavailable is the part of the foods which can be utilized in the body [4], calcium is bioavailable if it can be absorbed and incorporated in bones [5].

In our study the Ca-enrichment of instant coffee has been carried out taking into consideration the low Ca-

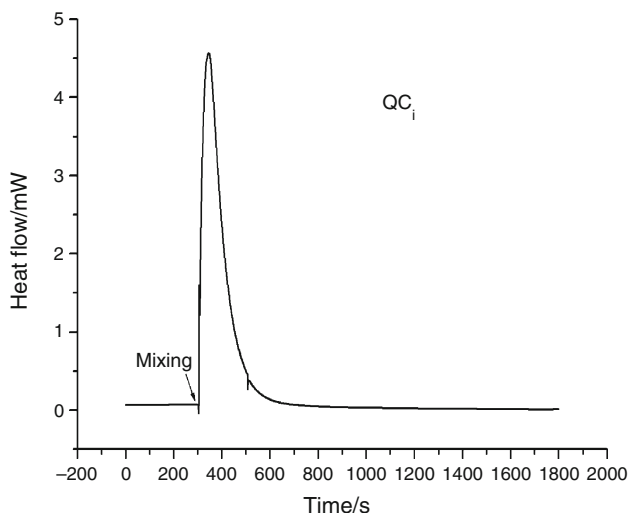


Fig. 3 The isotherm solution curve of instant fresh cheese whey powder enriched in calcium (QC_i)

content (about 1 g/kg) of coffees, only one-third of their phosphorus content, and also the fact that the caffeine of coffees further increases discharge of Ca from the body. At Ca-enrichment of instant coffees it must have also been considered that the ‘solubility’ of the additive should be almost the same as that of the instant coffee.

Materials and methods

For Ca-enrichment, the sour whey powder (fresh cheese whey powder) enriched in Ca-malate, -lactate and -citrate trade named Kalcima[®] QC and being under EU patentization

[6] has been used. Its main characteristics are shown in Table 1.

Kalcima[®] QC due to its composition and colloid-chemical structure can be instantized (QC_i), so its colloid-chemical solubility is probably close to the solubility of instant coffee powder. Kalcima[®] QC and QC_i seem to be additive-foods, bioavailability of their Ca has been proved by clinical examinations [7]. As a coffee product, the instant coffee (Nescafé Classic, producer: Nestle Hungária Co. Ltd.) (DE) has been used. Into the comparative study the Hungarian produced calcium-malate (CaM)—Pécsi Milker Co. Ltd.—has also been involved.

In our experiments 20–20 mg from calcium-malate (CaM), fresh cheese whey powder enriched in Ca (QC), its instant version (QC_i), instant coffee (DE), mixture of 50% instant coffee (DE) and 50% instant fresh cheese whey powder enriched in Ca (QC_i) (the mixture denoted by DEQC_i) were measured separately into the bottom of a mixing batch vessel (in case of reference vessel 20 mg water) and 180 mg distilled water into the upper part of it. The samples were put into a SETARAM Micro DSC-II calorimeter. In 5 min after attaining the heat balance the two parts of the cell have been mixed and the isotherm solution curves have been detected at 20 °C. By the integration of the curves the enthalpies, i.e., heat amounts liberating at solution, have been determined.

Results and discussion

In Fig. 1, the isotherm solution curve of CaM is shown. The dry mass of sample was 20.48 mg, and the total mass was 200.12 mg. It is obvious from the Fig. 1 that the solution is a

Table 2 The most important measured (*m*) and calculated (*c*) values of the isothermic DSC-curves of solution of additives used for calcium enrichment (CaM, QC and QC_i)

Values of DSC-curve	Denomination of sample		
	CaM	QC	QC _i
<i>m</i>			
Solution's			
Start/s	398 ± 25	295 ± 20	300 ± 20
End/s	8315 ± 140	6750 ± 100	868 ± 60
1st maximum/s	730 ± 40	473 ± 30	346 ± 20
2nd maximum/s	–	1883 ± 80	–
Area under curve			
Enthalpy/Jg ⁻¹	-2.56 ± 0.16	-2.88 ± 0.18	-2.29 ± 0.12
<i>c</i>			
Range of solution/s	8315 ± 140	6455 ± 90	568 ± 50
1st maximum from start of solution/s	332 ± 20	178 ± 16	46 ± 8
2nd maximum from start of solution/s	–	1588 ± 60	–
Enthalpy of dry sample/Jg ⁻¹	-25.0 ± 1.2	-27.8 ± 1.4	-23.4 ± 1.2

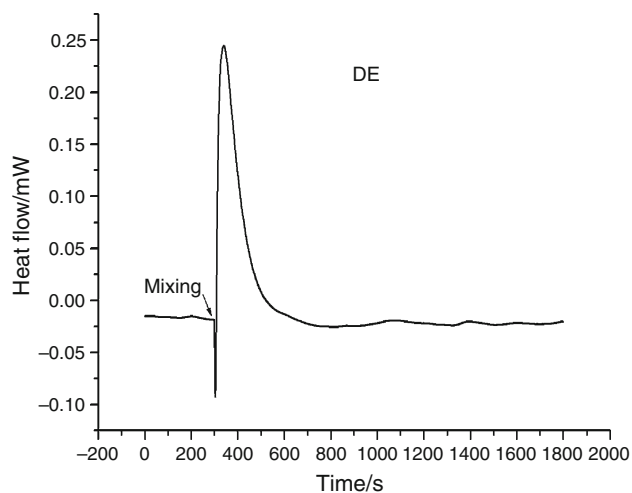


Fig. 4 The isotherm solution curve of instant coffee powder (DE)

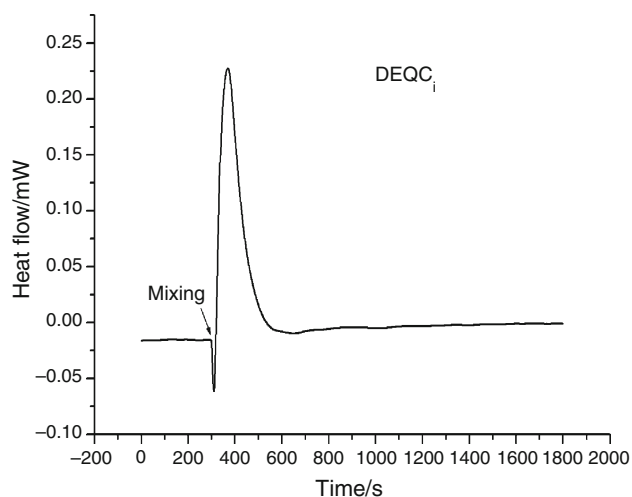


Fig. 5 The isotherm solution curve of a mixture of 50% of instant coffee powder (DE) and 50% instant fresh cheese whey powder enriched in Ca (QC_i) (denoted as $DEQC_i$)

heat-producing process. By analyzing the curve it can be stated that the starting time of solution is at 398 s, its end is at 8315 s, and the maximum is at 730 s. The enthalpy calculated from the area under the curve for the dry mass is -2.56 J/g (the negative sign refers to the exotherm process in case of SETARAM equipments).

In Fig. 2, the isotherm solution of fresh cheese whey powder enriched in calcium (QC) is shown. The measured mass of sample was 20.21 mg, and the total mass was 195.18 mg. It can be seen in Fig. 2 that the solution may be divided into two steps, the first is probably the fraction richer in CaM, and the second is richer in fresh cheese whey powder. The beginning of the solution is at 295 s, its end is at 6750 s, the first maximum peak is at 767 s, and the second is at 2177 s. The enthalpy—normalised for dry mass—calculated from the area under the curve is -2.88 J/g.

In Fig. 3, the isotherm solution of instant fresh cheese whey powder enriched in calcium (QC_i) is shown. The dry mass of sample was 19.95 mg, and the total mass was 203.73 mg. It is obvious from Fig. 3 that the solution is a quick, one-component exotherm process. The starting time of solution is at 300 s, it completed at 868 s, and the maximum of the heat production is at 346 s. The enthalpy calculated from the area under the curve and corrected for the dry mass is -2.29 J/g.

Table 2 contains the most important parameters of Figs. 1, 2 and 3 and the values were calculated based on them. From the data of Table 2, the followings can be concluded:

- the heat amount liberating at the solution of the three samples is approximately the same,
- the solution also begins after about the same time,
- by an order of magnitude less time is necessary to the solution of the instant sample and
- the instant sample reaches the maximum of its solution within a significantly shorter time.

The instant version of the fresh cheese whey powder enriched in calcium (QC_i) is very probably suitable to the Ca-enriching of the quick-soluble instant coffee powder on the basis of the results of our investigations. For the sake of proving it Figs. 4 and 5 are demonstrated. In Fig. 4, the isotherm solution curve of instant coffee powder (DE), and in Fig. 5 that of 50–50% mixture of instant coffee powder and instant fresh cheese whey powder enriched in Ca ($DEQC_i$) are shown.

It is obvious from Figs. 4 and 5 that the solution of both samples is of one-phase, quick process, and the slope of the curves is the same.

Conclusions: applicability

On the basis of the results instant coffee products enriched with calcium using Kalcima QC_i were made, and marketing survey was carried out with them. The following instant coffees were involved in examinations.

A: Caffeine-free corn chicory coffee. Ca:P ratio = 0.24:1

C: 'MACI' caffeine-free coffee. Ca:P ratio = 0.14:1

E: Nescafe 3 in 1 Classic. Ca:P ratio = 0.13:1

Ca:P ratio of all three variations were set at 1:1 by adding Kalcima QC_i of the following concentrations

B: +2.31%

D: +0.81%

F: +1.13%.

Marketing survey was carried out in three big Hungarian cities (Budapest, Debrecen and Kaposvár) involving focus groups.

In summary, it can be stated that the participants did not find any difference between the solution of different sample-pairs. As regards, the sensory appeal from amongst the three sample-pairs at A–B and C–D sample-pairs the Ca-enriched samples B and D were found to be better. From the sample-pairs even at a higher price the B (21%), D (46%) and F (33%) would be bought instead of samples without Ca-enrichment and having a lower price.

The recent study well fit to our former investigations [8, 9] where we could demonstrate the availability of isoperibolic technique to solve different food-physics problems in the field of research and development.

Acknowledgements This study has been carried out in the framework of project BAROSS-DD07-DD-KKV-07-2008-0005/OMFB-00463/2009 supported by the Hungarian State. The SETARAM Micro DSC-II was supported by grants OTKA C272 (for D. L.).

References

1. Dworschák E. Food-nutrient. What we have to know on our nutrition. Budapest: Mezőgazdasági Kiadó; 1985. p. 1–141.
2. Szakály S. Kalcium-Tejtermék-Egészség (Calcium-Dairy Foods-Health). Budapest: G-Print Nyomda; 2001. p. 1–119.
3. Szakály S. Étrendi kalcium és humánegészség (Dietary Calcium and Human Health). Budapest: G-Print Nyomda; 2005. p. 1–68.
4. O'Dell BL. Bioavailability of trace elements. *Nutr Rev.* 1984;42: 301–8.
5. de Vrese M, Scholz-Ahrens K, Barth CS. Bioavailability of calcium. *Bull IDF.* 1991;255:33–42.
6. Keller B, Schäffer B, Szakály S. Sour whey powder enriched in calcium and its production and utilization in foodstuffs. Patent EP 2175736 (2008).
7. Szakály S, Figler M, Keller B, Schäffer B. A kalciumban dúsított túrósavó-por bioaktivitásának klinikai vizsgálata (Clinical examination of bioavailability of fresh cheese whey powder enriched in calcium). *Tejgazdaság (Dairy J).* 2008;68:13–9.
8. Schäffer B, Keller B, Lőrinczy D. Application of isotherm calorimetry in the development of foods containing probiotic live flora and enriched with bioavailable Ca²⁺. *J Therm Anal Calorim.* 2009;95:703–8.
9. Schäffer B, Keller B, Daróczi L, Lőrinczy D. Examination of growth of probiotic microbes by an isoperibolic calorimetry. *J Therm Anal Calorim.* 2010;102:9–12.