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high pressures

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Abstract

The solubility of CO₂ in milk was studied at temperatures of 25, 38 and 50°C and at pressures up to 6.9 MPa using a static method with an accuracy of 5%. These data are important for the design and control of processes which use CO₂ for precipitation of casein from milk.

The solubility of CO₂ in milk was found to increase with pressure and decrease with increasing temperature — a trend similar to that observed for the solubility of CO₂ in water. At 25°C, the solubility of CO₂ in milk was less than the solubility in water over the entire pressure range studied. Precipitation of casein was not observed. At 38°C and 50°C and pressures greater than 5.5 MPa, complete precipitation of casein from milk was observed, and the solubility of CO₂ in milk was approximately the same as that in water. This indicates that casein destabilization is accompanied by an increase in water available for dissolution of CO₂. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Casein; CO₂; Solubility data; Solubility measurements; Proteins

1. Introduction

The use of CO₂ in food processing is becoming increasingly important because it is non-toxic and environmentally safe compared to the solvents it replaces. Supercritical CO₂ extraction of valuable components from food or food components [1] is probably the best known application of CO₂ in food processing. The use of CO₂ for other applications in food processing is fairly recent [2–4].

In one such application, Tomasula et al. [3,4] precipitated casein from milk in batch and continuous processes using high pressure CO₂ at 38°C and 5.5 MPa. Skim milk contains about 9% total

solids; comprised of minerals, casein (2.5%) and whey proteins (0.5%), and lactose. It has a pH of 6.6. Casein, one of the principal functional food proteins, is an ingredient in a wide variety of products, such as baked goods, imitation cheeses, coffee creamers, texturized meats and snacks. Industrially, it is used in products such as glues and adhesives [5].

Casein precipitates from milk at its isoelectric point of pH 4.6 and at temperatures >6°C [5]. Casein is precipitated from milk commercially at temperatures >30°C through the addition of an acid, such as HCl, to its isoelectric point [6]. Temperatures >30°C ensure that a cohesive curd is obtained thus minimizing processing losses. A cohesive curd can easily be separated from the whey, be washed and dried. The whey proteins do not precipitate under these conditions.

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Casein is comprised of submicelles linked together by colloidal calcium phosphate (CCP) and hydrophobic bonds. Addition of acid to milk causes the CCP to solubilize from the casein micelles destabilizing the structure and resulting in casein precipitation. The nature of the precipitate obtained is temperature dependent and is believed to result from the hydrophobic interactions [5].

Use of CO₂ as a precipitant, instead of HCl, is attractive because it is eliminated from the whey on release of pressure. When CO₂ is sparged into milk, it dissolves in the endogenous water of milk and hydrolyzes water to form carbonic acid. With increasing pressure the solution pH drops, CCP solubilizes and casein precipitates. On release of pressure, CO₂ is evolved and the final pH of the casein and whey are 5.8 and 6.0 respectively [3]. CO₂ does not contaminate the casein or whey after precipitation, unlike HCl which remains in the whey. Casein precipitated from milk with HCl requires washing before further processing.

The process discussed in this paper is not to be confused with the gas antisolvent process (GAS) by which supercritical or high pressure CO₂ is used as an antisolvent to induce precipitation from an organic solvent [7,8]. This method has also been used to recover insulin [9] by dissolving it in DMSO and then using CO₂ as the precipitant. The protein precipitates because CO₂ expands DMSO reducing its effectiveness as a solvent for the protein. Recovery of the protein entails procedures for solvent removal and for prevention of protein redissolution. In our process, casein does not redissolve because it has been modified during precipitation.

Equipment and process design, as well as process simulations, for applications of CO₂ in food processing require solubility data for CO₂ in foods or their components. There is a large body of experimental data in the literature on the solubility of CO₂ in water at a variety of temperatures and pressures [10–15]. Data for the solubility of CO₂ in foods or biological materials is scarce [16].

More recently, Singh et al. [17] showed that the solubility of CO₂ in gelatinized starch is less than that in water but approached its solubility in water at high pressures. These data, as well as data for the diffusivity of CO₂ in starch, were necessary to understand the supercritical CO₂–starch system as

well as to provide fundamental data for the design and control of processes with CO₂ injection or mixing in starch-based processes.

In the design of a new method for continual removal of casein from a high pressure system after precipitation from milk using CO₂, Tomasula et al. [4] assumed that the solubility of CO₂ in milk was equal to the solubility of CO₂ in water. An economic analysis [18] comparing the cost of this precipitation step using CO₂ to that using HCl showed that liquified CO₂ was fairly expensive — at an average price of \$70/ton [19] — compared to HCl if the CO₂ was not recovered and reused. Knowledge of CO₂ solubility in various foods would provide more accurate estimates of the costs associated with CO₂ processing.

In this paper, we use a saturation-type method to measure the solubility of CO₂ in milk at three temperatures and over a range of pressure. The method was evaluated using measurements of the solubility of CO₂ in water for comparison.

2. Experimental

2.1. Apparatus

The batch vessel used in this study has been described previously [3] and was used in these studies with some modification. The experimental apparatus is shown in Fig.1. CO₂ in a cylinder equipped with a dip tube (BOC, Murray Hill, NJ), chilled to 6°C, was allowed to flow freely to the batch reactor or was pumped using a Model DSF-B52 Haskel pump (Haskel, Inc., Burbank, CA) if the desired pressure exceeded approximately 5.9 MPa. System pressure was monitored using a Model PDCR-9 pressure transducer (Druck, Inc., New Fairfield, CT) with an accuracy of ±0.1%. Thermocouples were used to record system temperature, jacket temperature and ambient temperature. Temperature variations during a run were of the order ±0.3°C. Pressure and temperature readings were directed to a datalogger.

After the vessel was filled with milk the lid was secured. A vacuum pump (Model DD100, Precision Instruments, Chicago, IL) was used to evacuate the associated piping of the reactor. After a run, the milk–CO₂ mixture was isolated between

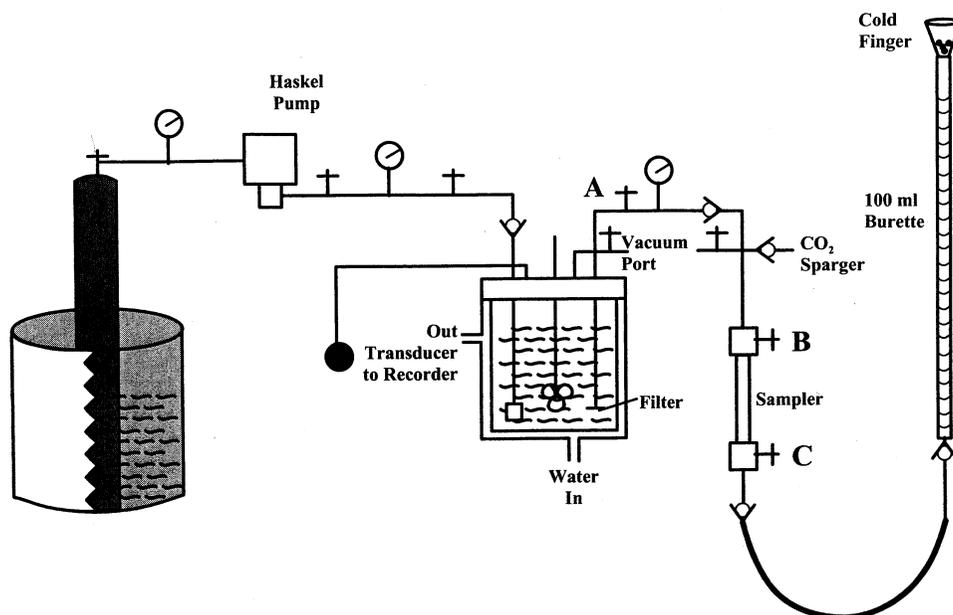


Fig. 1. Apparatus used for the solubility measurements.

valves B and C. The sampler volume was 11.0 cm^3 . The volume of the sampler was determined by weighing the amount of water at 25°C which filled it and converting the weight to volume using the density of water [20]. The sampler was constructed from a length of nominal 1.3 cm tubing with a wall thickness of 0.12 cm. A 100 ml buret, with a cold finger to prevent evaporation of water, was used to measure the amount of CO_2 dissolved in the milk. The volume was measured with an accuracy of $\pm 0.03 \text{ ml}$. The solids content, as weight percent, of the liquid sample collected in the buret after each run was determined using a Mark 1 Moisture Analyzer (Denver Instrument Co., Arvada, Col) and was converted to moisture content by subtracting from 100. Barometric pressure was determined using a barometer (Precision Thermometer & Instrument Co., Philadelphia, PA) with an accuracy of $\pm 0.254 \text{ mm Hg}$. The buret temperature was measured using a calibrated glass thermometer with an accuracy of $\pm 0.03^\circ\text{C}$.

2.2. Solubility studies

In a typical run, the reactor was filled with 750 ml of skim milk. The associated piping of the

reactor was evacuated until a reading of 1 torr was indicated on a vacuum gauge (Vacuum Research Corp., Model 902097). Vacuum was then applied to the headspace of the reactor and the contents of the reactor were evacuated while stirring rapidly to remove air [13]. The stirrer remained on throughout the experiment. The reactor contents were heated to 25, 38 or 50°C by hot water flowing through the jacket of the reactor. CO_2 was admitted to the reactor to flush its headspace. A back-pressure of approximately 0.30 MPa was then placed on the reactor while CO_2 was allowed to saturate the reactor and its contents. CO_2 was then sparged into the reactor until the desired pressure was reached. Pressures up to 6.9 MPa were used. The reactor contents were then allowed to equilibrate for 2 h. A series of preliminary experiments using residence times up to 8 h showed that steady state was achieved in less than 2 h. After this time, valve A (Fig. 1) was opened and the liquid contents of the reactor were drawn through a filtered tube into the sampler between valves B and C. The filter screened out any small casein particles which may have formed. Valve B was then closed and valve C was opened to expand the sample into the buret. The volume of liquid in the

buret was not read until the foam, if any, subsided. Fluid did not collect in the tubing between the sampler and buret because of the non-return valves in the line. After a run, the solids content of the fluid in the buret was determined. The experiments were done in triplicate.

2.3. Calculation of solubility

CO₂ evolved on expansion of the sample into the buret. Only milk or whey containing residual CO₂ remained in the buret. To calculate the solubility, the volumes of CO₂ and milk or whey in the 11.0 cm³ sampler at the temperature and pressure of the experiment were determined. The volume of CO₂ under experimental conditions was then converted to conditions of standard temperature and pressure (STP). In this study, STP was defined based on the temperature of the fluid in the buret and barometric pressure.

To determine the volume of CO₂ left in the fluid in the buret, the Bunsen coefficient for CO₂ in water [10], 0.759 at 25°C, was multiplied by the factor $(p_b \text{ mm Hg} - P_{vp})/760d_o$ to correct for the barometric pressure, p_b , and the vapor pressure of milk or whey, P_{vp} . The vapor pressures of milk and whey, based on the activity of water in milk of 0.993 [21], are equal to 23.59 mm Hg. d_o is the density of milk or whey [21]. If the fluid in the buret was white and casein precipitation was not observed in the reactor after depressurization, the density of milk was used in the correction factor calculation. A yellowish to clear fluid was an indication that some or all of the casein had precipitated. In this case, the density of whey was used in the correction factor calculation. The volume of CO₂ was then subtracted from the volume indicated on the buret to give the volume of milk or whey in the sampler. Subtracting the volume of the milk or whey from the volume of the sampler resulted in the volume of dissolved CO₂ at the temperature and pressure of the study. This value was corrected to STP after correction for the vapor pressure of water, barometric pressure and temperature and added to the volume of CO₂ calculated from the Bunsen coefficient. The solubility of CO₂ in the whey was converted to a water basis by dividing by the moisture content.

The non-ideality of the gas was represented using the compressibility factors given in [22]. Solubility of CO₂ in water is reported here as cm³ of CO₂ at STP/g of H₂O.

3. Results and discussion

In order to test the reliability of the experimental apparatus for determination of solubility, the solubility of CO₂ in water was determined at pressures of approximately 2.1, 3.5 and 6.9 MPa and at temperatures of 25, 38 and 50°C. Experimental results were reproducible to $\pm 5\%$ and were within 5% of the values given in Wiebe and Gaddy [10,11] and Houghton et al. [13]. Wiebe and Gaddy [11], using a similar sampling system, reported that the reproducibility of their data was $\pm 4\%$.

Fig. 2 shows the solubility of CO₂ in milk, expressed as cm³ of CO₂ at STP/g of H₂O, as a function of pressure. The curves showing the solubility of CO₂ in water obtained by Wiebe and Gaddy [10,11] and Houghton et al. [13] are plotted for comparison. Table 1 presents the solubility data for CO₂ in milk.

As shown in Fig. 2, the solubility of CO₂ in milk follows the same trends as the solubility of

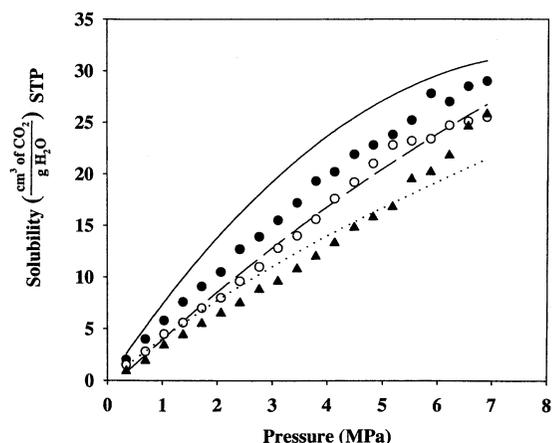


Fig. 2. Solubility of CO₂ in milk at: 25°C (●); 38°C (○); and 50°C (▲); and in water at: 25°C (—); 38°C (---); and 50°C (···) as a function of pressure. Solubility data for CO₂ in water are interpolated from the data of Wiebe and Gaddy [10,11] and Houghton et al. [13].

Table 1
Solubility of CO₂ (cm³ of CO₂/g H₂O) in milk as a function of pressure at 25, 38 and 50°C at STP

Pressure (MPa)	Temperature (°C)		
	25	38	50
0.34	2.0	1.5	0.90
0.69	4.0	2.8	1.9
1.03	5.8	4.5	3.4
1.38	7.6	5.6	4.4
1.72	9.1	7.0	5.5
2.07	10.5	8.0	6.5
2.41	12.7	9.6	7.5
2.76	13.9	11.0	8.8
3.10	15.5	12.8	9.6
3.45	17.2	14.0	10.8
3.79	19.3	15.6	12.0
4.13	20.2	17.6	13.3
4.48	21.9	19.2	14.8
4.82	22.8	21.0	15.8
5.17	23.8	22.8	16.8
5.51	25.2	23.2	19.5
5.86	27.8	23.4	20.2
6.20	27.0	24.7	21.8
6.55	28.5	25.1	24.6
6.89	29.0	25.5	25.8

CO₂ in water. The solubility of CO₂ in milk increases with pressure at a constant temperature and decreases with temperature at a constant pressure.

The solubility of CO₂ in milk at 25°C is lower than its solubility in water over the entire pressure range studied. Its value as a percentage of the solubility in water was approximately 77% at low pressures increasing to over 90% at the higher pressures. Casein precipitate was not observed in the vessel following depressurization at any value of pressure. Also, the corresponding sample in the buret was still milky, another indication that casein did not precipitate.

At 38°C, as shown in Fig. 2, the solubility of CO₂ in milk is approximately 20% of that of water up to 3.5 MPa. Negligible amounts of casein precipitate were observed in the vessel after the experiments were completed. The whey was milky in appearance at the lower pressures but became yellowish as pressure approached 3.5 MPa. At pressures >3.5 MPa, casein precipitation was complete and the whey was clear. The solubility

of CO₂ in milk is approximately equal to its solubility in water within $\pm 5\%$. Similar trends were noted at 50°C but at 5.5 MPa, the solubility of CO₂ in milk is greater than its solubility in water by approximately 15%. However, at 50°C the reproducibility of the solubility data was $\pm 10\%$ at pressures >5.5 MPa.

At all temperatures, the gradual approach of the values for solubility of CO₂ in milk to those for the solubility of CO₂ in water is indicative of changes in the solvation of the casein micelles as pH decreases (or pressure increases). Fox et al. [5] report that the casein micelles in milk are highly solvated with approximately 2 g of H₂O/g casein. Famelart et al. [23] reported solvation (g of H₂O/g casein) at 20°C as a function of pH. The pH was adjusted through addition of acid to milk, not CO₂. As the pH was decreased from 5.5 to pH 4.5, there was a linear decrease in solvation as pH approached 4.5. Solvation approached a minimum of 1 g of H₂O/g casein. Famelart et al. [23] also reported that milk treated by high pressure alone showed enhanced solvation, but pressures in their study exceeded 250 MPa. It was postulated that the high pressures reduced micelle size. It is doubtful that the much lower pressures of this study had as significant an impact on solvation. Decreased solvation is expected at the higher temperatures though, as interactions among the casein micelles increase.

In a recent study [24], it was shown that precipitation of casein using CO₂ was complete at 0.1 pH units higher than it was for precipitation with HCl. This indicated that there may be slight pressure effects on the solubilization of CCP, but these effects were linked to various interactions of calcium, phosphate and bicarbonate ions in the whey.

It is apparent from the results obtained in this study that solubility data for the CO₂-H₂O system may be used to estimate the solubility of CO₂ in milk provided that casein precipitation has begun, usually at pressures exceeding 4.1 MPa, because the solubilities are nearly the same. This assumption has been used in process calculations [4] and in cost estimation studies [18]. Because pooled milk was used in this study, variations in the

solubility of CO₂ in milk due to variations in the source of milk were not observed.

4. Conclusion

The solubility of CO₂ in milk was determined at temperatures of 25, 38, and 50°C and pressures up to 6.9 MPa. The solubility was lower than the corresponding solubility in water under the same conditions, except where casein was present; typically, at pressures greater than 3.5 MPa. At pressures >4.1 MPa, solubility models for the CO₂-H₂O system may be used to simulate the solubility of CO₂ in milk in process simulators, calculations or in cost estimation studies.

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