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New Gushing Mechanism Proposed by Applying Particle Size Analysis and Several Surfactants

The complex phenomenon of gushing occurring in carbonized beverages has been investigated in order to better understand the mechanism and to give input for further research to introduce preventive measures for the industry. The knowledge that microbubbles are stabilized through surface active substances, and in this form can induce gushing, was used to examine a selection of representative surfactants. For the analysis, a particle size distribution method was used which enabled to detect particles at nanometer level, starting from 0.8 nm onwards. The experiments using pure aliphatic surfactants (DTAC, TTAC, CTAC, ODTABr, CPC, SDS, and Tween 20) revealed that only CTAC, solved in CO_2 containing table water at 2 g/l (above the critical micellar concentration), induced gushing. CTAC therefore was characterized as gushing typical by its structure (length of hydrophobic part and kind of head group). Gushing caused by CTAC was not only observed through shaking of the bottles, but also without any shaking at all. The latter observed fact was not explainable by the mechanical incorporation of CO_2 bubbles stabilized by CTAC monomers, but generally through stabilized microbubbles formed by a mechanism that is yet unknown. The particle size analysis revealed that particles grow, starting from ca. 10 nm to reach several 100 nm, if sufficient amounts of CO_2 molecules are present. The growth was accelerated by a mild shaking of the bottles. The results pointed out that CTAC micelles grow by diffusion of CO_2 molecules into the hydrophobic core. Thereby, microbubbles are formed and stabilized through CTAC monomers at the interface gas/liquid, and can grow to gushing-relevant sizes of several 100 nm.

Descriptors: gushing, particle size distribution, surfactant, hexadecyltrimethylammonium chloride (CTAC), micelle growth, carbon dioxide diffusion, stabilized microbubbles

1 Introduction

The gushing phenomenon occurring in the brewing and beverage industry is a quality aspect that needs to be coped with. Experiences made so far have shown that the effect of spontaneous overfoaming of bottled, carbon dioxide containing, beverages such as beer cannot be explained monocausally but by different, intervening factors, contributing to the complexity of this phenomenon [1–6]. For beer, as a product example, in principle two groups of gushing triggers are currently under discussion. Particles such as calcium oxalate or fine kieselguhr are made responsible as a cause for secondary gushing. Cereal raw materials used for production of beer, qualitatively changed due to fungal infestation during some years and in specific regions, have been explained as the cause of primary gushing [7–9]. Recently, two new hypotheses in terms of the chemical nature and origin of primary gushing have been formulated. Two classes of proteins, fungal specific hydrophobins and plant typical non-specific lipid transfer proteins (ns-LTPs) were identified as gushing positive [10–13]. In contrast polar lipids excreted by *Fusarium* showed a gushing reducing effect [14].

Furthermore, there has been an agreed assumption for a common mechanism of gushing induction in the form of stabilized microbubbles, once these bubbles have reached a critical diameter [15–17]. Microbubbles are stabilized by an agglomeration of surface active substances at the interface gas/liquid of the microbubbles that are incorporated into the liquid by shaking the bottles. Upon pressure release in the system, e.g. by opening the bottle, the stabilized bubbles grow. This growth is determined by parameters such as bubble radius, surface tension and gas concentration. Efforts made previously to entirely elucidate the gushing mechanism and in turn to prevent gushing are bound to the fact that numerous different surface active substances are involved in the stabilization of microbubbles [7]. For this reason, our research was designed to obtain further insights in the gushing mechanism with particular emphasis on gushing inducing substances and, thereby, to work out explanatory approaches of the gushing mechanism. Substances with known chemical structure and which have the capacity to induce gushing should be found in pure form. This would help to better understand and describe the gushing mechanism. In contrast to complex molecules, these substances should preferably have a simple structure, which brings the advantage that the mechanism of gushing induction can be better elucidated from the chemical point of view. Thereby, substances relevant for gushing are likely to be easier identified by their chemical characteristics, so start-

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Tables and figures see Appendix

ing points for further investigations and suggestions for counter measures can be introduced, e.g. the avoidance of emergence of relevant substances or their elimination from the beverage matrix. The industry has always shown interest in such measures in order to effectively avoid gushing, as this phenomenon is considered a product fault and, thus, results in a loss of image [6,18,19].

For our experiments, the principles of known methods for analyzing the gushing potential of malt have been considered. These methods are the gushing rapid test, also known as the Weihenstephaner test, and the modified Carlsberg test [20-23], which are acknowledged and applied during quality assurance procedures by the brewing industry. Applying the last procedural part of the modified Carlsberg test we studied the effect of selected surfactants on the development of gushing in Bonaqa® water samples. The measurement of particle size distribution served as a tool for elucidating the gushing mechanism. The measurements were applied at nanometer range, with the lowest detection limit of 0.8 nm, which previously had not been performed to the best of our knowledge in connection with gushing.

2 Materials and methods

2.1 Chemicals

All chemicals used for the analytical measurements were of p.a. quality. Sodium azide, prepared exclusively from a standard solution (c = 100 g/l), served as an antimicrobial agent and was added to the Bonaqa® bottles. The following process steps such as shaking and opening the bottles were performed according to the modified Carlsberg test as described in MEBAK [23]. The Bonaqa® water samples were obtained from a special filling and contained larger amounts of CO_2 than the normal Bonaqa® products available on the market. The CO_2 content was measured by using a tester of Haffmans B.V. (type CBL-04) at 20 °C in a water bath. The CO_2 content amounted to 7.4 g/l. Table water of Bonaqa Classic (1 l) consists of the following contents: hydrogen carbonate (381 mg), magnesium (28 mg), calcium (68 mg), sodium (180 mg), chloride (259 mg).

Several surfactants as representatives within different classes were observed for their gushing behaviour: As cationic aliphatic surfactants served dodecyltrimethylammonium chloride (DTAC), tetradecyltrimethylammonium chloride (TTAC), hexadecyltrimethylammonium chloride (CTAC) and octadecyltrimethylammonium bromide (ODTABr); as a cationic, aromatic, aliphatic surfactant, cetylpyridinium chloride (CPC) was chosen, whereas sodium dodecyl sulfate (SDS) served as an anionic aliphatic surfactant, and Tween 20 as a non-ionic surfactant. The surfactants in powder form were purchased from Sigma Aldrich, except for Tween 20, which in liquid form came from Merck.

2.2 Preparation of surfactants in Bonaqa® water for examining their gushing characteristic

The examination of surfactants for their gushing inducing characteristics was carried out by adding a prepared surfactant/water solution into carbonized table water. The bottle samples were proceeded as in accordance with the modified Carlsberg test [23]. Changes in the procedure are explained while discussing the results. In brief, following procedure was applied: Amounts of surfactant powder or solution were weighed into a beaker and distilled water was added. The beaker was shaken gently to support the dissolution of the powder. The solution was transferred into a volumetric flask (25 ml) and filled with distilled water until the mark. Further to that, 25 ml of the Bonaqa® water sample (4 °C) was substituted with the surfactant solution (25 ml) after pipetting of sodium azide solution (1 ml, c = 100 g/l) into Bonaqa® water. The bottle was then corked and turned one time for 180 degrees. The bottles were then shaken horizontally for 3 days using the instrument VKS-75 Control from Edmund Bühler GmbH (frequency: 1.25 Hz, stroke length: 0.05 m). Afterwards, the bottles were left standing for 10 min, then three times turned manually (180 degrees) within 10 s, and after 30 s standing opened.

For the correct interpretation of the results, it should be noted that overfoaming in low amounts of around 10 g, for example, after opening the bottle cannot be accepted as typical gushing behaviour. Only distinct overfoaming can be defined as gushing coming from the gushing mechanism.

2.3 Particle Size Analyzer

A Nanotrac Particle Size Analyzer (with the measurement range between 0.8 to 6500 nm) from Microtrac was used to determine the particle size distribution. The analyzer allows the detection of all particles present in the medium that differ in the refraction index of the liquid. The intensity of the dynamic straylight is graphically depicted as the intensity sum distribution in dependency of the particle size. Existing particle sizes are recognized by the slope in the graph, while in a horizontal course, the corresponding particle sizes are not present. The steeper the slope, the higher the amount of particles detected, taking the logarithmic scale into account.

For the depiction of the distribution, 20 single measurements were performed consecutively to provide an arithmetic mean for each class of particles, including confidence intervals with a probability of P = 0.95. The Student's t-test was performed to work out statistical significance [24]. In all figures the confidence intervals have been omitted for reasons of clarity.

2.4 Preparation of different CTAC/Bonaqa® solutions for the particle size measurement

2.4.1 *CTAC/Bonaqa® solution containing CO_2*

In the CTAC/Bonaqa® solutions (2 g/l) containing CO_2, the particle sizes were measured under CO_2 pressure in a prepared pressure cell, in which the sensor of the particle measurement instrument is integrated. The bottle containing the solution is directly linked to the pressure cell via a tap mechanism to achieve constant CO_2 pressure conditions at $p > p(CO_2 \text{ equilibrium})$, as a decrease of the system pressure leads to foaming which can change the particle size distribution. Therefore, only the particle size distribution in CTAC/Bonaqa® was captured without any pressure decrease, causing unwanted CO_2 release and foam formation, in order to reflect the gushing development only by this particle size distribution. All measurements were performed without movement of the solution. For practical reasons only one bottle can be used for obtaining either the particle size distribution or the overfoaming amount.

2.4.2 CTAC/Bonaqa® solution poor in CO_2

The Bonaqa® water in the bottles containing CO_2 was decarbonized by heating until 70 °C and cooling down to 20 °C. The heating temperature of 70 °C at atmospheric pressure leads to a significant reduction of the CO_2 content, so that the decarbonized Bonaqa® water is poor in, but not entirely free of CO_2 [25]. The decarbonized water (305 ml) was refilled into the bottles. 1 ml of sodium azide solution (c = 100 g/l) and the prepared solution (25 ml) were added to reach the final concentration of the CTAC/Bonaqa® solution of 2 g/l. The bottles were corked up and were either shaken (according to the modified Carlsberg test) or not shaken at all. In the bottles, atmospheric pressure prevailed (pressure free condition) and, therefore, the measurement of the particle size distribution can be performed in the bottle.

3 Results and discussion

3.1 Investigation of surfactants to their gushing inducing capacity

Referring to models of amphiphilic substances stabilizing microbubbles [7,11], aliphatic surfactants as one part of gushing-relevant substances have been investigated. As representatives of cationic aliphatic surfactants, dodecyltrimethylammonium chloride (DTAC) and hexadecyltrimethylammonium chloride (CTAC) have been selected. The compound cetylpyridinium chloride (CPC) served as the respective aromatic representative, while sodium dodecyl sulfate (SDS) as anionic and Tween 20 as non-ionic surfactant. The concentration range of application was chosen to reach the level of either below, close to or above the critical micelle concentration (CMC), so that the presence of only monomers as well as micellar aggregates could be examined for their gushing inducing capacity. The end concentration of applied surfactant/Bonaqa® solution are shown in Table 1.

While applying CTAC, no overfoaming for c < CMC (0.1 g/l) was observed. At a concentration of slightly above CMC (0.5 g/l), a marginal overfoaming (6 g) was induced. A further increase to 1 g/l generated a marginal overfoaming (11 g) as well. At a concentration significantly above CMC (2 g/l), however, gushing (80 g) was induced. With CTAC a surface active substance has been found, which, by 80 g overfoaming, significantly induces gushing above the CMC. The observation that gushing is only induced from a certain concentration of surface active substances was made previously, investigating hydrophobins [26]. CTAC can be taken as an example that with an increased concentration, the overfoaming amount increases as well. In comparison to CTAC, overfoaming for DTAC, SDS and Tween 20 at increasing concentrations (c > CMC) was not observed (Table 1) and, thus, a gushing-relevant capacity such as for CTAC could not be established for these surfactants.

So far, it is demonstrated that gushing was induced by CTAC after shaking the bottles for 3 days. In the next experiment we aimed at examining whether gushing is induced by CTAC also without shaking the bottles and therefore without the mechanical incorporation of CO_2 into the solution (c = 2 g/l). The results are shown in figure 1.

After performing the process for 30 min without shaking, only a slight foam formation was observed (the bottles were warmed up to 20 °C in a water bath). After 1 day standing at room temperature, an overfoaming amount of approx. 10 g was obtained. After leaving the bottles for 7 days at room temperature, an overfoaming amount of approx. 50 g was measured, which comes close to the gushing result of 80 g, detected after 3 days of shaking (Table 1). This demonstrates that CTAC added to Bonaqa® caused gushing without shaking. Therefore, in our experiments, the presumption that stabilized microbubbles are formed by mechanical incorporation of microbubbles into the liquid and agglomeration of surface active substances at the bubbles` interface, could not be confirmed for CTAC in this case. The results applying CTAC have shown that without shaking, and therefore without the introduction of CO_2 gas, gushing was induced with overfoaming amounts (7 days standing) comparable to the shaken sample (Table 1). It must be assumed that another mechanism for the formation of stabilized microbubbles exists. From the fact that gushing was not induced immediately due to the addition of CTAC after 30 min, but was observed to a minor degree after 1 day and to a larger extent after 7 days, it can be concluded that the new gushing mechanism requires time to form stabilized microbubbles. The knowledge obtained so far points out that the new mechanism can be explained by the characteristics of the CTAC micelles.

Already referred, an increase of the overfoaming amount for SDS, Tween 20 and DTAC at increasing concentrations (c > CMC) was not observed, after shaking the bottles for 3 days (Table 1) and, thus, a gushing-relevant capacity such as for CTAC could not be established for these three surfactants. DTAC and CTAC are within the same homologous series and differ only in terms of the number of carbon atoms at the hydrophobic part of the molecule. This tail of the gushing surfactant CTAC consists of in total 16 C-atoms, while DTAC only possesses 12 C-atoms. In order to establish a relationship between the gushing behaviour of aliphatic cationic surfactants and their CH-chain length, two further surfactants were chosen that show either two lesser or two more carbon atoms compared to CTAC in their CH-chain, which are tetradecyltrimethylammonium chloride (TTAC) and octadecyltrimethylammonium bromide (ODTABr), respectively. It cannot be ruled out that counter ions have an influence on the thermodynamic process of micellar aggregation of the alkyltrimethylammonium ions [27,28]. Except for one, the cationic surfactants used in these experiments originate all from the same homologous series, possessing chloride as the identical counter ion (DTAC, TTAC and CTAC); only ODTABr possesses bromide as the counter ion. The results for these surfactants (TTAC and ODTABr) have shown that no overfoaming was observed after 3 days of shaking, even at concentrations above CMC (Table 1). As CTAC induces gushing only at a concentration above CMC, as soon as micelles have been formed in sufficient amounts, then CTAC micelles in contrary to their homologous neighbours, must possess distinct characteristics that can be described as gushing typical (e.g., the CH-chain length of the monomers) with the experimental conditions in mind.

By applying another aliphatic cationic surfactant, cetylpyridinium chloride (CPC), which in structure is similar to CTAC (16 C-atoms), possessing however a different head group, but also chloride as counter ion, we aimed at examining in which way the structure in the head group can have an influence on the overfoaming behaviour. The results show that with increasing concentrations of CPC above CMC, no overfoaming was observed after shaking the bottles for 3 days (Table 1), despite the identical CH chain length as CTAC. In addition, it seems that CPC micelles do not possess the gushing characteristics like the CTAC micelles.

This notably demonstrates that particular gushing attributes of micelles are not only depending on the CH chain length, but furthermore on the constitution of the molecules` head group. At this point it should be noted, that the influence of the medium, consisting of carbonized tap water and sodium azide, might have an influence on the micellar aggregation of the applied surfactants. But it is safe to assume that these possible influences can be neglected, as gushing became apparent far above CMC, and thus sufficient amounts of micellar aggregates were likely to be formed [27,29]. As CTAC was the only surfactant contained in our model solution, it is therefore clear that present micelles were formed by only this one type of substance, so that the micelles have a homogenous composition [28,30,31].

The aim of further investigations was to examine the steady development of gushing at certain time points during shaking of the bottles, and observing the mechanism leading to the formation of stabilized microbubbles. For this, the measurement of the particle size distribution served as a tool.

3.2 Particle size distribution of CTAC/Bonaqa® solution depending on shaking time

For CTAC, the concentration of 2 g/l was chosen which caused significant gushing after shaking for 3 days (Table 1). For this experiment, the prepared bottles were not turned manually, so that in this way no CO_2 could be introduced. The bottles were shaken horizontally according to the modified Carlsberg test. The particle size measurement was at first carried out after the substitution (20 min, without shaking at all) (Fig. 2). The following measurements were taken for the bottles shaken for 1, 3 and 4 days, respectively (Fig. 2). The confidence intervals in Fig. 2 have been omitted for reasons of clarity. For these measurements, they have been relatively small throughout so that the differences were distinct and significant, apart from the cross sections in the graph.

After 20 min standing, an increase in particle size from 3 to 9 nm was observed. A further small increase around 100 nm followed. A similar course is shown after 1 day of shaking, observing a large part of particles in sizes between 1 and 3 nm. It is assumed that detected particles between 1–2 nm pertain to CTAC monomers, which might be in a status of dynamic equilibrium with micellar aggregates [27]. The micelles may be about 3 to 9 nm in sizes. After 3 days of shaking, also particles within 1–2 nm (monomers) and 3–9 nm (micellar aggregates) became visible. Novel is that from 9 nm onwards, up to 200 nm, a further steady increase of the size distribution can be recognized, which demonstrates that particles had been developed after 3 days of shaking, while this was not the case to this extent after 1 day of shaking. After 4 days shaking, also particles with 3–9 nm in sizes (micellar aggregates) became visible. It is new that after 4 days of shaking, larger particles with 40 nm up to ca. 6000 nm occurred increasingly, while sizes between 9–40 nm, observed after 3 days of shaking, were hardly detected, taking the slight confidence intervals into account. When comparing the results of particle sizes of each sample according to shaking time, a continuous increase of particles, starting from ca. 10 nm up to ca. 6000 nm, could be observed. Larger particles became present after 3 days, which had not been detected after 1 day of shaking. The smaller part of this particle fraction decreased significantly, or vanished completely after 4 days of shaking, and larger particles up to approx. 6000 nm became increasingly present. The results lead to the new assumption that shaking influences particles, present in the solution and, thereby, a continuous increase of particles occurs, starting from the sizes of 3-9 nm. These particles might be CTAC micelles which have the ability to grow. An explanation for this growth can be given by a process that is characterized by diffusion of CO_2 molecules into the hydrophobic core of the micelles. Due to the fact that larger particles were observed only after 3 days of shaking, which can be attributed to growing micelles, it can be assumed that the process of CO_2 diffusion needs time to develop. This assumption is indirectly confirmed by previous experimental results (Fig. 1; CTAC samples were not shaken at all). Real gushing could be observed only after a certain standing time of the bottles, presumably when sufficient stabilized microbubbles in respective sizes were present. The results show further that after 4 days of shaking, most of the micelles (40 %) have a size of 50 to 200 nm. These sizes are in accordance with the results for gushing-relevant bubbles as mentioned by *Fischer* [16]. The author described that through membrane filtration of beer samples (0.1 μm pore size), the gushing affinity of unfiltered beers could be entirely suppressed. The gushing affinity could be halved by applying pore sizes of 0.45 and 0.65 μm.

3.3 Further experiments (particle size analysis) for confirming the hypothesis of a new gushing mechanism

Further examinations were conducted to test the new mechanism, assuming that micelles start growing by CO_2 diffusion until becoming gushing-relevant. For this, the following considerations served as a basis:

- We have shown (Fig. 1) that gushing can occur without shaking by applying CTAC (2 g/l). Therefore, it should be examined if micelles grow up to gushing-relevant sizes without shaking the samples.

- In CO_2 poor water, the diffusion process of CO_2 into the inner cell may not take place for all micelles present in the medium. Therefore, it should not be the case that micelles start to increase in amounts compared with ones in CO_2 containing water.

In order to examine the growth of micelles in water containing CO_2 and without shaking, one bottle was left standing for 4 days and measured for particle size distribution under pressure at $p > p$ (CO_2 equilibrium). The results obtained (Fig. 3) were compared to those of the bottle shaken for 4 days, which had been examined previously (Fig. 2). For the experiment with CTAC/Bonaqa® sample poor in CO_2 one bottle was shaken for 4 days and the other one was left standing for 4 days (Fig. 3).

Particles within the fraction of 3–9 nm (micellar aggregates) could be ascertained for all samples (Fig. 3). As already shown previously (Fig. 2), the particle size distribution, after 4 days of shaking for the sample containing CO_2, increased from ca. 40 nm up to ca. 6000 nm. No shaking but standing for 4 days of the CTAC/Bonaqa® solution containing CO_2 has also led to the development of particles with the similar size range (between ca. 50 and 200 nm) as observed for 4 days shaking, but in lower amounts. The existence of this particle fraction (stabilized microbubbles) demonstrate that micelles grew to these sizes (after 4 days without shaking the bottles). A comparison of particle fractions by looking at the interval between 50 and 6500 nm of the two CO_2 containing CTAC/Bonaqa® samples, reveals a capture of 60 % of particles in the shaken sample, while only 20 % in the non-shaken sample. Therefore, horizontal shaking favours the development of larger particles.

For the samples poor in CO_2 only a slight increase of the size distribution at between approx. 50 and 200 nm was observed, so that larger particles are barely existent in water poor in CO_2. In comparison to the samples containing CO_2, this size fraction is negligible and assumingly can be deduced from lowest amounts of CO_2 remained in the decarbonized Bonaqa® water, which caused the growth of only some micelles. From this point of view no growth of micelles can be expected without CO_2. The particle size distributions of CTAC/Bonaqa® solution (2 g/l) poor in CO_2, shaken for 4 days and not shaken but left standing for 4 days, are nearly identical. As there is no difference, the shaking of the CTAC/Bonaqa® solution poor in CO_2 has no positive influence on the growth of particles. Therefore, for the development of larger particles (stabilized microbubbles) sufficient CO_2 amount has to be available for the CO_2 diffusion process, so that sufficient micelles grow to sizes relevant for gushing.

4 Conclusion

With CTAC, a new surface active and gushing-relevant substance is discovered, which possesses a simple chemical structure. CTAC has caused distinct overfoaming in carbonized water at a concentration above the critical micelle concentration (CMC). Through the examination of similar surfactants, which under the same conditions provided gushing negative results, the characteristics of CTAC as to length of the hydrophobic part and kind of the head group could be figured out as typical for gushing with respect to the experimental conditions. The result that gushing starts to develop primarily after a longer time period (without shaking) cannot be explained by the incorporation of microbubbles stabilized by surface active substances agglomerating at the bubbles` surface. Therefore, a new gushing mechanism for the formation of stabilized microbubbles is indicated. From the observation that gushing starts to occur once the micellar concentration reaches a critical value, it can be assumed that the micelles already present in the system can most likely be made responsible for the induction of gushing. In this respect, the particle size distribution method served well as an analytical tool in order to formulate a new hypothesis for a mechanism of gushing development. Only by the presence of CO_2 a notable increase of greater particles of up to several 100 nm could be observed, which furthermore was enhanced by the process of shaking. The cognitions obtained so far from our experiments lead to the hypothesis that micelles start growing upon diffusion of CO_2 molecules into the hydrophobic inner cell part, so that stabilized microbubbles in sizes of several 100 nm are formed, which induce gushing.

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Appendix

Table 1 **Overfoaming amount caused by the surfactants in Bonaqa® water (according to the modified Carlsberg test) in dependence of the surfactant concentration (Surf. conc.). Surfactant concentrations were chosen as to either under, close to and above the critical micellar concentration (CMC)**

	Cationic surfactants in the same homologous series												Surfactants of other classes							
Surfactant	DTAC			TTAC		CTAC				ODTABr			CPC			SDS		Tween 20		
CMC*	22.2 mmol/kg [28]			5.6 mmol/kg [28]		1.4 mmol/l [30]				0.043 mmol/l [32]			0.79 mmol/l [33]			8.2 mmol/l [34]		0.071 mmol/l [35]		
Mw [g/mol]	264			291.94		320.01				392.52			358			288.38		1227.7		
CMC** [g/l]	5.81			1.61		0.45				0.02			0.28			2.36		0.09		
Surf. conc. [g/l]	1	2	9	1	2	0.1	0.5	1	2	0.02	0.1	0.45	0.5	0.7	1	1	3.5	0.1	0.5	1
Overfoaming [g]	0	0	0	0	0	0	6	11	80	0	0	0	0	0	0	6	1	0	1	0

* CMC derived from the literature

** CMC calculated as derived from the literature and the molecular weight

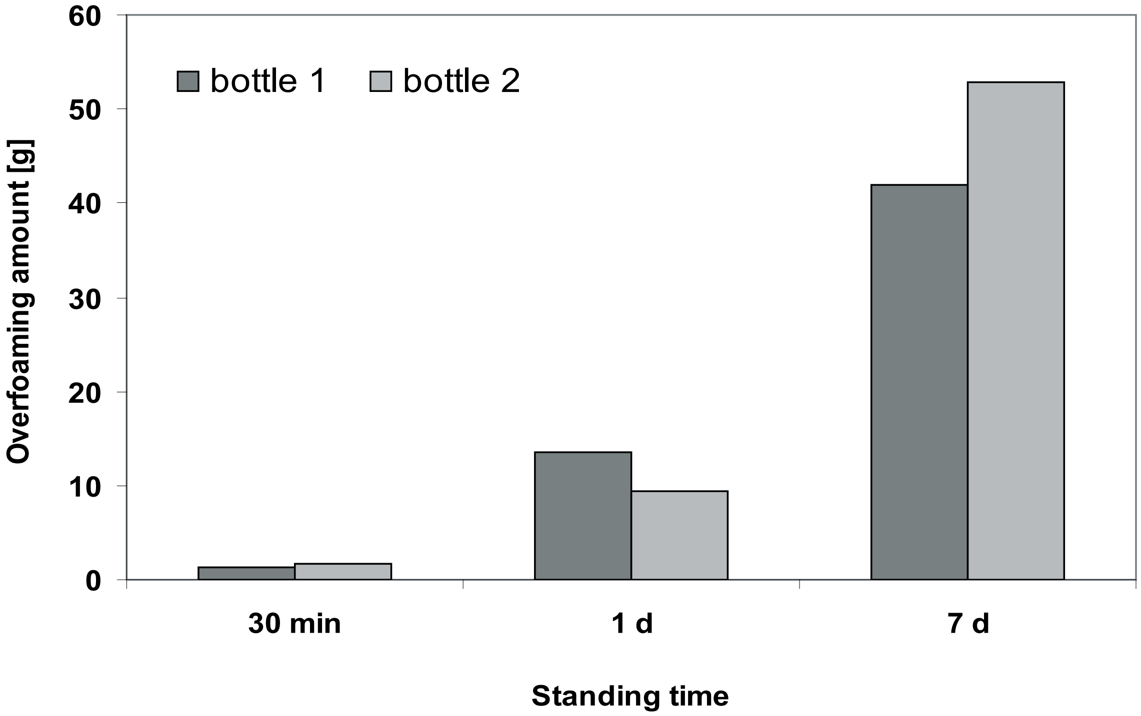

Fig. 1 **Overfoaming amounts of CTAC/Bonaqa® solution (2 g/l) in two bottles according to standing time (without shaking). The bottles were identical samples to obtain two values**

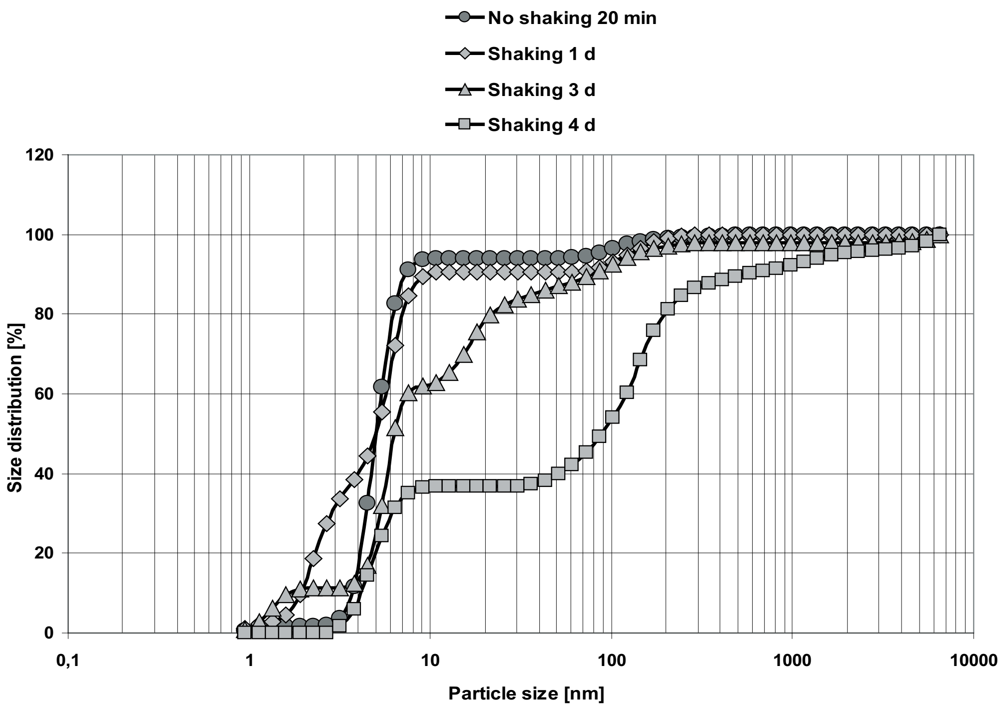

Fig. 2 Particle size distribution of CTAC/Bonaqa® solution (2 g/l, above CO_2 equilibrium pressure) in relation to shaking time

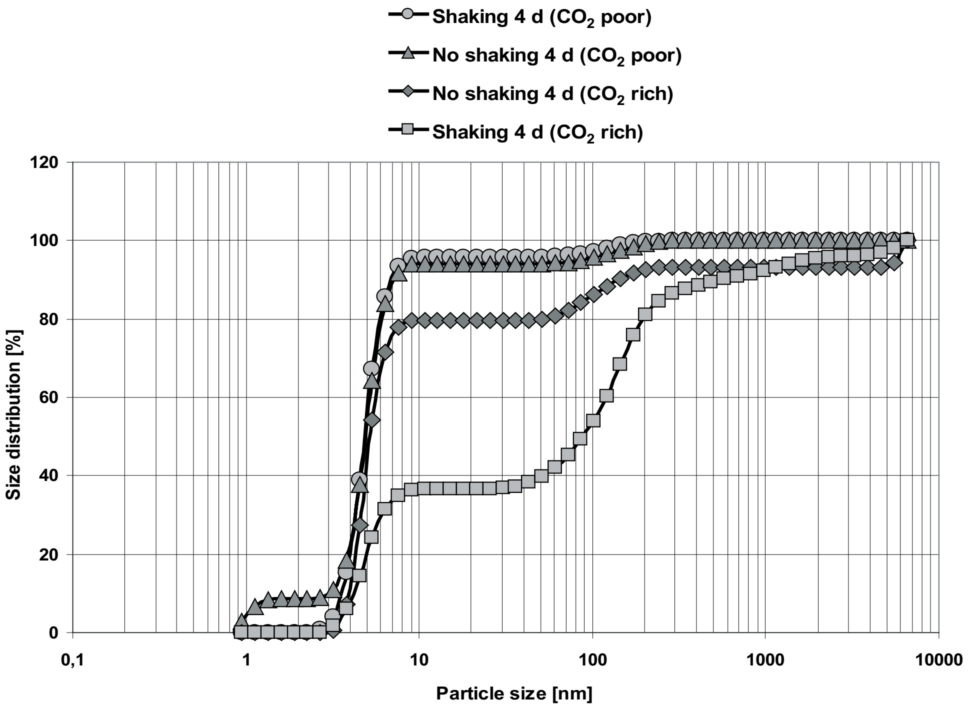

Fig. 3 Particle size distribution of CTAC/Bonaqa® solution (2 g/l, above CO_2 equilibrium pressure) in relation to conditions of shaking (according to the modified Carlsberg test) and of CO_2 content; the size distribution of the sample containing CO_2 with 4 d shaking is extracted from figure 2