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# Impact of Accelerated Shelf-life Tests on Physical Stability of Beverages Based on Weighted Orange Oil Emulsions

Emulsions play an important role as concentrated semi-finished products for the preparation of soft drinks and also other beverages such as beer-based mixed drinks (shandies) and liquors. The determination of the physical stability of the finished product is of great interest in the development of new beverage emulsions. For practical purposes, it is barely possible to examine the beverages along the expected shelf-life in real time. Accelerated storage tests are therefore widely used in the beverage and flavor industry to obtain information on visual instability phenomena like turbidity loss, creaming (“ringing”) or sedimentation. However, a systematic approach to evaluate the instabilities enhancing storage conditions and a standard procedure is missing. In this study different storage conditions (extrinsic factors) were compared with regard to their impact on the physical changes of emulsion-based beverages: elevated temperature (40 °C) with and without light exposition (40 °C, 5000 Lx) and periodic agitation (12 h/d). To induce the instability phenomena within a fraction of an assumed shelf-life of 6 months, artificial product defects (intrinsic factors) were incorporated into a standard formulation of a weighted orange oil beverage emulsion: reduction of the emulsifier concentration (–50 %), reduction of the weighting agent concentration (–66 %) and weakening of the homogenization process. The results reveal that due to instabilities of the emulsions all accelerating storage conditions have remarkable but different effects on the rate and extent of deterioration. Elevated temperature storage as well as a light box accelerate physical deterioration of beverage emulsions by a factor of 5.8 to 9.6 resulting in a similar loss of turbidity in just a fraction of the normal shelf-life. Periodic agitation speeds up deterioration even faster (accelerating factor 7.7–11.0), but with greater deviations in the extent of deterioration to real-time tests and consequently a complication of a prediction.

Descriptors: Beverage emulsion, turbidity, colloidal stability, accelerated shelf-life tests, forced ageing

## 1 Introduction

Beverages and mainly soft drinks often consist of beverage emulsions in order to incorporate water insoluble flavors (flavor emulsion), to imitate the cloudy appearance of natural juice and color (cloud emulsion) or both combined [1, 2]. Compared to other oil-in-water food emulsions, beverage emulsions are a unique class of type, as they are highly concentrated semi-finished products and after being processed into drinks finally consumed considerably diluted [3]. However, in both states, concentrated and diluted, the emulsions have to be stable for a certain period of time (e.g. 6–12 months)[4, 5]. In order to prevent physical changes of these emulsions, significant effort is made by employing stabilizers and intensive mechanical forces [6]. In spite of these efforts the physical instability is a great issue in the development of new formulations.

The reason is due to the inherent instability of beverage emulsions as generally known from macroemulsions. In addition, governmental regulations restrict the application of stabilizing ingredients [7]. Thus, new formulations always have to be analyzed in terms of physical stability beside chemical and sensory evaluation leading to time-consuming development processes. The industry consequently employs techniques to accelerate these changes, the so called accelerated shelf-life tests (ASLT) [8–10]. As a result, various stability tests combined with diverse analytical methods were developed making outcomes difficult to compare. Therefore selected ASLTs were examined and compared in this study to get information about their impact on physical deterioration of beverages with weighted orange oil emulsions.

Citrus flavors are by far the most popular of all flavors, thus citrus oils (orange oil, lemon oil) are part of many beverage formulations. These essential oils mainly consist of terpene hydrocarbons (e.g. limonene, myrcene, linalool) in addition to a large number of volatile compounds like aldehydes [11]. Citrus oils have a low polarity and therefore have to be emulsified to become water soluble. Those beverage emulsions are macroemulsions characterized by droplet sizes in the range of 200 nm to a maximum of 1 µm [12]. In contrast to nanoemulsions (50 to 200 nm) and microemulsions (10 to 100 nm, made with low-energy homogenization methods)

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macroemulsions are always cloudy and thermodynamically not stable. Nevertheless, macroemulsions can achieve kinetically stable state [6, 13].

To prevent coalescence of oil droplets, emulsifiers are needed to stabilize the oil-water interface. The most common emulsifiers for beverage emulsions are gum arabic and sodium octenyl succinate starches (OSA starch). These polysaccharide based surfactants have the ability to form a thick hydrophilic interfacial layer around oil droplets and provide stability against aggregation mainly through steric repulsion [14]. In contrast to triacylglycerols, which can be found in most food emulsions, citrus oils have a certain solubility in water which provokes Ostwald ripening. This instability process occurs when the dispersed phase contains more water-soluble lipids which leads to growth of the large droplets at the expense of smaller ones due to diffusion of lipids through the water phase [15]. To prevent the oil from diffusing into the water phase high amounts of the mentioned emulsifiers, i.e. ratios of 1:1 or more are used [16–18]. Nevertheless, when using citrus oils as the only component in oil phase, Ostwald ripening is a major problem for physical instability of beverages. This can be prevented by the use of highly hydrophobic substances, so called “ripening inhibitors”. These additives are added into the oil phase in order to generate an entropy of mixing effect that counteracts the driving force of Ostwald ripening [19]. Glycerol ester of wood rosin (ester gum) are normally used as a weighting agent to increase the density of the oil phase. By matching density of oil and water phase, separation of the oil phase (creaming) can be slowed and shelf-life can be extended [20]. In addition, ester gum can also act as a ripening inhibitor as it is highly insoluble in water [21]. As mentioned, the use of these stabilizers can be limited due to governmental or sensorial reasons and physical instabilities can still be an issue.

That is why various ASLTs, also called “forced ageing”, have been developed by food and pharmaceutical industries to which *Mizrahi* gives an overview [10]. ASLTs assume a kinetic model for the deterioration process that may be a chemical, physical, biochemical or microbial process. The case-dependent measure of the deterioration is a function of time, intrinsic (compositional) factors and extrinsic (environmental) factors [10]. Only the extrinsic factors are sensible working points for enhancements in ASLTs since the intrinsic factors and herewith composition of the product are the objects of ASLTs investigations. As most of the deterioration processes in food products are derived from microbial or (bio) chemical processes, many of the described ASLTs are not useful for emulsion stability tests emphasizing the physical instability mechanisms. Concentrated beverage compounds and emulsions are a highly specified group of semi-finished products. Therefore, companies in the beverage and flavor industries individually designed own tests for new product development and quality control. There are a number of different storage tests which are proprietary, with restricted access. Consequently the range of enhancing test conditions are widely spread: elevated temperature storage at 37 °C up to 55 °C for 4 to 8 weeks, thermal cycling, agitation and light boxes [12, 18, 22]. The strategies to combine tests with measurements for evaluation of stability are different, too. These include measurements of turbidity, droplet size distribution or zeta potential, microscopic analysis and visual examination [8, 9].

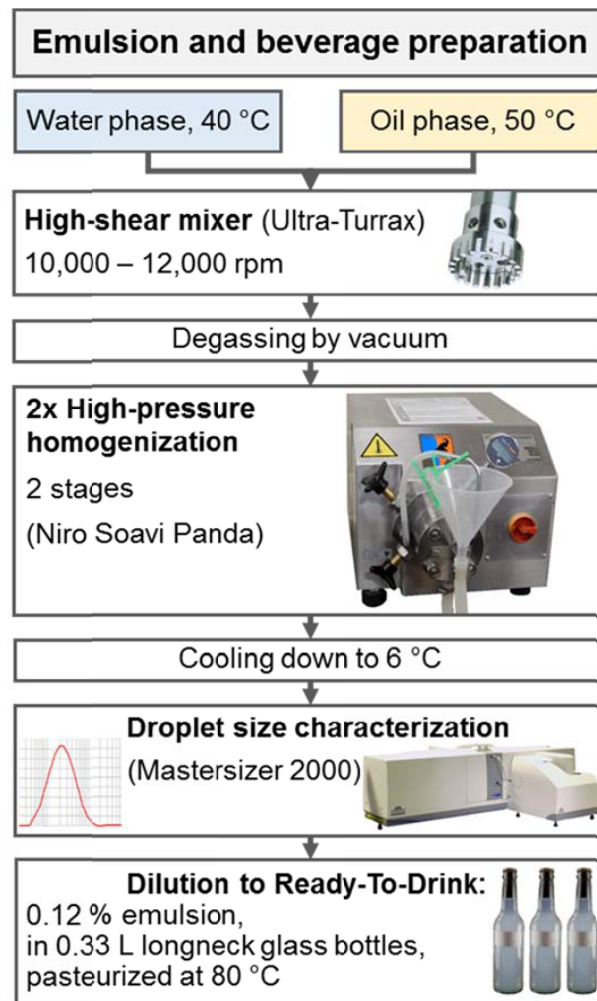


Fig. 1 Preparation of the emulsions and beverages

The objective of the present study is to comparatively quantify techniques for accelerating physical deterioration of beverage emulsions. Therefore a standard beverage emulsion formulation was used and specifically changed to promote typical instability mechanisms.

## 2 Materials and Methods

### 2.1 Ingredients

As ingredients for the emulsions concentrated orange oil (5-fold) was used as the oil phase, which was weighted with glycerol ester of wood rosin (ester gum). An OSA starch selected from the Purity Gum® range for beverage emulsions was provided by Ingredion (Hamburg, Germany) and used as emulsifier. Citric acid monohydrate and sodium benzoate were used to microbiologically stabilize the emulsions as well as the beverages. Furthermore beverages were prepared with sucrose and filtered tap water. Emulsions were produced with deionized water.

### 2.2 Emulsion preparation

To enhance the physical instability mechanisms during ageing of the beverages, a formulation for a standard flavor emulsion (reference

**Table 1** Artificially created product defects, the physical relations and the expected instability phenomena in the finished beverages

Artificial product defect	Related emulsion quality deficiencies	Expected physical instability phenomenon
Reduced ester gum concentration	High density gradient oil / water phase, higher solubility of oil phase in water phase	Ostwald ripening, creaming
Low homogenization pressure	Larger oil droplets, high droplet size span	Creaming
Reduced emulsifier concentration	Weak interfacial film	Aggregation, coalescence

emulsion) was modified by integrating artificial “product defects” as shown in table 1. These interventions in the intrinsic factors lead to specific deficiencies in emulsion quality that can be associated with specific instability mechanisms.

All beverage emulsions were made in accordance with the following procedure, which is also shown in figure 1. The intervention in the intrinsic shelf-life factors of the formulation and the homogenization are described in table 2. Oil and water phase were prepared first by dissolving the ester gum in the orange oil at 50 °C and the emulsifier, citric acid and sodium benzoate in water at 40 °C, respectively. After allowing the emulsifier to fully hydrate overnight, emulsions were produced in three steps. First a coarse pre-emulsion was prepared by combining the oil phase and the water phase with an IKA Ultra-Turrax high-shear mixer (Staufen, Germany) at 10,000 to 12,000 rpm for 1 min to achieve emulsion droplets of around 10 µm. To remove air bubbles and foam the emulsions were degassed by vacuum before homogenizing with a GEA Niro Soavi Panda high-pressure homogenizer (Parma, Italy). The homogenizer is equipped with two stages which were set according to table 2. Homogenization pressures are always indicated in the form: pressure 1<sup>st</sup> stage/pressure 2<sup>nd</sup> stage. Emulsions were analyzed for droplet size distribution by laser diffraction within 2 h after preparation and then stored at 6 °C until further processing.

The density of the oil phases were measured with an Anton Paar GmbH DMA 5000 digital density meter (Graz, Austria). The oil phase of the reference emulsion had a density of 959.3 ± 0.2 kg/m<sup>3</sup>, the oil phase with less weighting agent (ester gum) had a density of 878.0 ± 0.5 kg/m<sup>3</sup>. The beverage base to which the emulsions were added had a density of 1041.0 ± 0.1 kg/m<sup>3</sup>. All emulsions were produced twice for a double investigation.

### 2.3 Beverage preparation

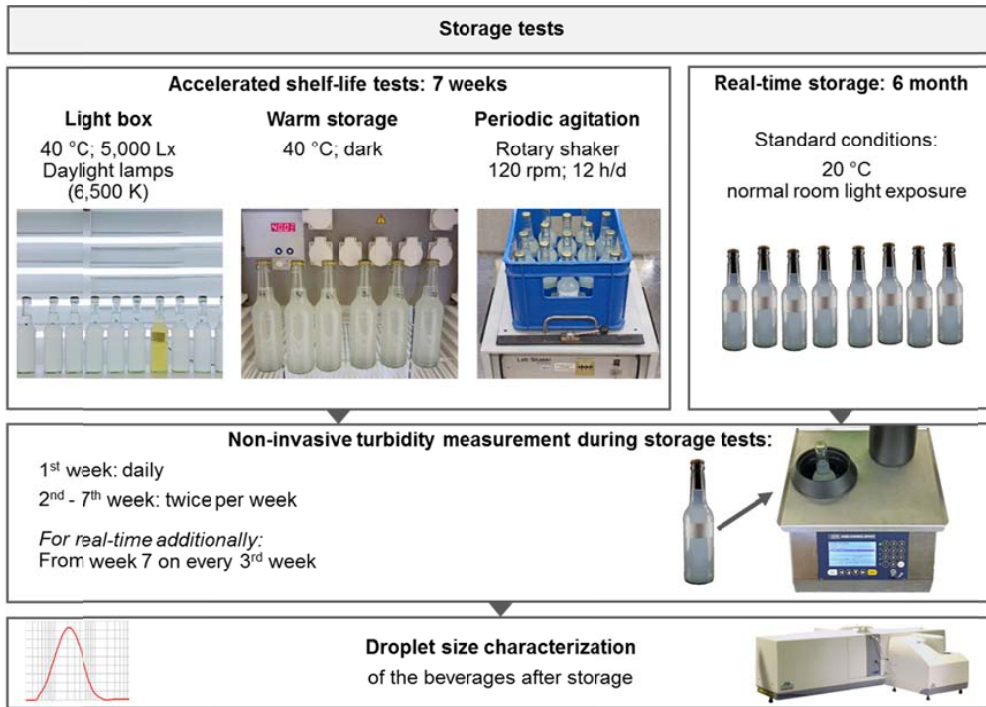
The Ready-To-Drink beverages were made 24 h after preparation of each emulsion according to the following formulation: sucrose (10 %), citric acid monohydrate (0.2 %), emulsion (0.12 %) and filtered tap water (q.s. 100 %). Beverages of each emulsions were filled in 0.33 L-long-neck white glass bottles without UV barrier. To prevent physical and optical spoilage caused by microbial growth, all samples were pasteurized in a pasteurization unit (PU)-controlled bottle pasteurizer at 80 °C reaching 10 PU (z = 10 K).

### 2.4 Accelerating storage conditions

A modification of the environmental conditions (extrinsic factors) were employed to realize the ASLTs. To evoke instabilities in the emulsions and the beverages, the sample bottles were exposed to the defined storage conditions by means of a light box with controlled temperature and illumination, a thermostat cabinet (Aqualytic, Dortmund, Germany) and a laboratory orbital shaker (Braun, Melsungen, Germany), which are shown in figure 2 (see next page). Three different storage conditions were realized: 40 °C at 5000 Lx illuminance, warm and dark storage at 40 °C and periodic agitation of 12 h/d at 20 °C. For the agitation the bottles were placed upright in a crate with dividers and shaken at an oscillation frequency of 120 rpm. Three bottles of each beverage were exposed to the respective storage conditions for 7 weeks. All beverages were examined daily in the first week and twice per week from the second week onwards for the following characteristics: turbidity and visual appearance, namely sedimentation, flocculation or ringing. In addition three bottles of all beverages were stored at 20 °C under normal room light exposure for 6 months (defined as “standard conditions”) to evaluate the accelerating factors of the ASLTs. For the long-term storage at standard conditions intervals

**Table 2** Interventions in the intrinsic shelf-life factors of the formulation of beverage emulsions with artificially promoted instabilities (product defects); % in wt%

Ingredients	Reference emulsion	Emulsion with artificial product defects		
		Reduced ester gum concentration	Low homogenization pressure	Reduced emulsifier concentration
Orange oil	6.0 %	10.0 %	6.0 %	6.0 %
Ester gum	6.0 %	2.0 %	6.0 %	6.0 %
OSA starch	12.0 %	12.0 %	12.0 %	6.0 %
Citric acid monohydrate	0.3 %	0.3 %	0.3 %	0.3 %
Sodium benzoate	0.1 %	0.1 %	0.1 %	0.1 %
Deionized Water	75.6 %	75.6 %	75.6 %	81.6 %
Homogenization 1 <sup>st</sup> valve/2 <sup>nd</sup> valve	2 x 300/50 bar	2 x 300/50 bar	1 x 250/50 bar	2 x 300/50 bar



**Fig. 2** Schematic procedure of the storage tests and the examination of the deterioration during storage through non-invasive turbidity measurement and droplet size characterization

for analyses were set to every third week until week 18 and a final measurement after 6 months. All bottles were opened for droplet size measurements after the respective storage time.

**2.5 Droplet size characterization**

The droplet size distributions were measured using a Malvern Mastersizer 2000 laser light scattering system (Malvern Instruments, U.K.). Emulsions were analyzed directly after preparation and as Ready-To-Drink beverages at the end of storage time. All samples were gently shaken before measurement. In order to achieve an obscuration of the laser beam between 4 % and 6 % the concentrated emulsions were diluted 500-fold with deionized water. After the storage time the final beverages with emulsions were diluted with deionized water 1:1 for analysis. For the calculation of the size distributions the following specifications were used: oil phase refractive index = 1.507 (absorption 0.001), dispersant refractive index = 1.330. For the samples with the oil phase containing a low weighting agent concentration (ester gum) the refractive index was 1.483. Droplet sizes are calculated and shown as fractional volume density distribution  $q_3$ .

**2.6 Turbidity measurement**

For the non-invasive turbidity measurements of beverages over the complete storage time without opening the bottles an Optek DT9011 laboratory turbidimeter (Optek-Danulat GmbH, Essen, Germany) was used. This turbidimeter features a triple beam scattered light optical design (590 nm–1100 nm wavelength), measuring forward (11°) and side (90°) scatter of the bottled product. In this study, only turbidity values of the side scattered light were used as this quantity is more sensitive to smaller droplets and corresponds more to the visual turbidity impression [23]. A sample analysis consists

of 250 single measurements while the bottle is rotating to ensure bottle defects like scratches, seams and differences in glass thickness have no influence on the measurement. Data analysis subtracts out corrupted values and calculates mean turbidity given in Formazine Turbidity Units (FTU). Two readings were taken for each sample (bottle) resulting in six values per emulsion and storage condition. The beverage base without emulsion served as a blank for turbidity measurements.

**2.7 Statistical analysis of the deterioration kinetics**

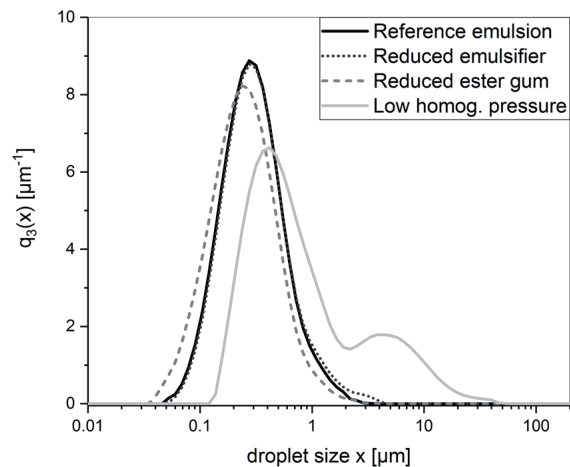
The physical deterioration phenomena investigated in this work can properly be inspected by the turbidity measurements as an objective measure of the visible changes during shelf-life. As the visible changes correlate with the side scattered light turbidity measurement the turbidity

of emulsions itself correlates with the droplet quantity and radius [24]. For a better comparability turbidity values (given in FTU) were standardized on the basis of the initial turbidity right after pasteurization and defined as normalized turbidity  $\tau$ .

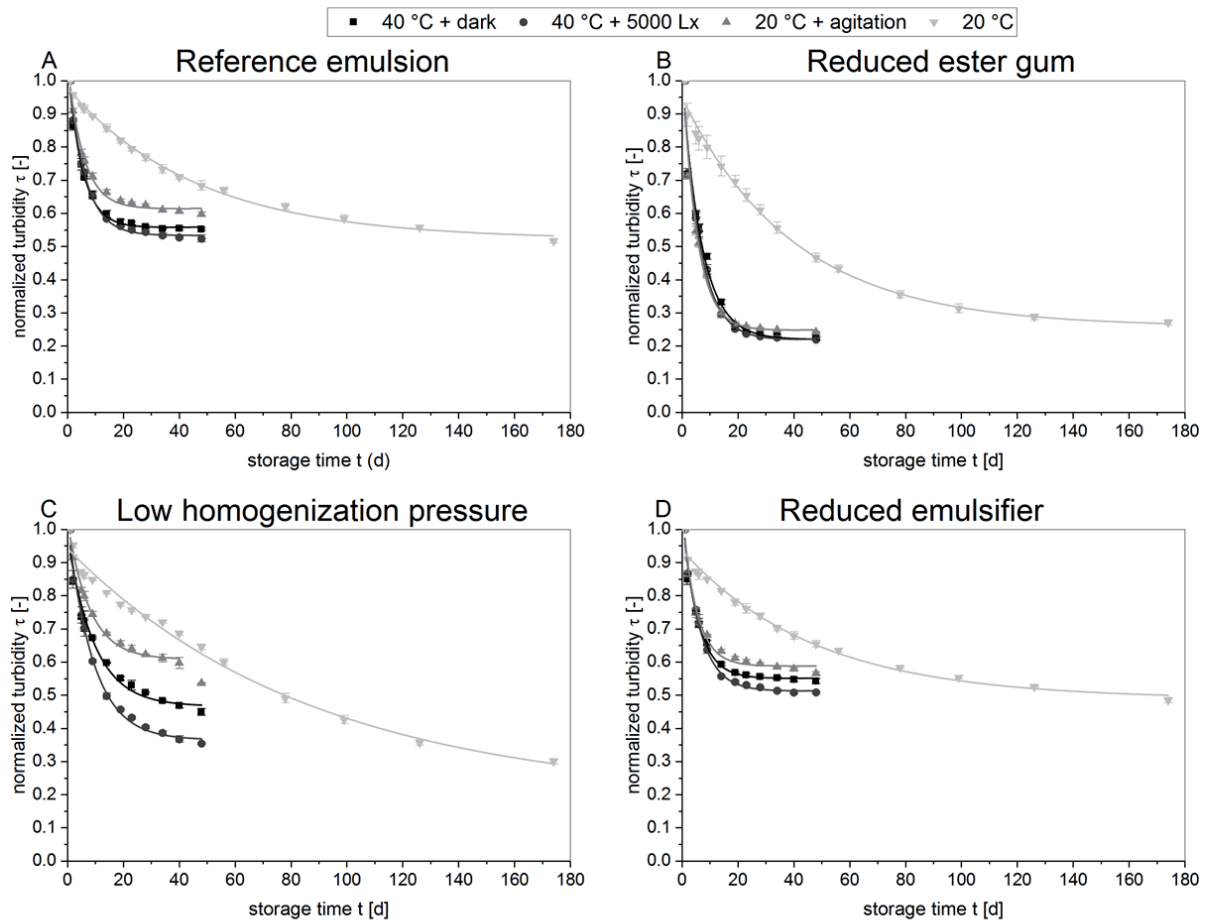
The deterioration follows thus an exponential decay function from the initial normalized turbidity  $\tau_0$  towards a kinetically stable minimum  $\tau^*$ . In an ideal experiment, the coefficient  $\tau'$  would be  $\tau' = \tau_0 - \tau^*$ .

$$\tau(t) = \tau^* + \tau' \cdot e^{-k \cdot t}$$

Whilst  $\tau^*$  can be taken as a measure for the extent of the deterioration enhancement, the constant  $k$  measures the deterioration



**Fig. 3** Droplet size distribution of the reference emulsion compared to that of the emulsions with artificial product defects: reduced ester gum concentration and emulsion homogenized with lower homogenization pressure



**Fig. 4** Normalized turbidity of beverages with different emulsions over storage time during accelerating and standard room conditions: **A:** reference emulsion, **B:** emulsion with reduced ester gum concentration, **C:** emulsion homogenized with lower homogenization pressure, **D:** emulsion with reduced emulsifier concentration

rate and is thus the most important indicator for the acceleration of the deterioration process. Therefore, the accelerating factor  $a$  is defined as the ratio of the deterioration rate constant under standard conditions without variation of the extrinsic factor in relation to the one under ASLT-conditions. However, when a precise prediction of the real-time storage under standard conditions is aimed, the  $\tau^*$  value of the ASLT is required and should preferably be equal to the  $\tau^*$  value under standard conditions. Although the precise prediction is not objective of this work, the parameters  $\tau^*$ ,  $k$  and  $a$  respectively are used to study and compare the impact of the storage conditions on the physical stability of beverages with weighted orange oil emulsions.

Statistical analyses including regression analysis were carried out using OriginPro 2017G (OriginLab Cooperation, Northampton, USA) to determine coefficients of determination, mean values and standard deviations.

### 3 Results and Discussion

#### 3.1 Characterization of the artificially weakened beverage emulsions

The emulsions were analyzed for droplet size distribution directly after preparation to ensure that changes in the emulsion formula-

tion did in fact cause the expected deficiencies in emulsion quality. According to figure 3, the reference emulsion shows a monomodal distribution of the droplet sizes between 50 nm and 1.1  $\mu\text{m}$ . The emulsion, which was homogenized only once at 250/50 bar, reveals a bimodal droplet size distribution with a small fraction of tremendously bigger droplets up to 30  $\mu\text{m}$ . The emulsion with reduced ester gum concentration shows a distribution slightly shifted to smaller diameters. As the viscosity of the dispersed phase decreases with reduced weighting agent concentration (ester gum), this result correspondent to findings of *Walstra* as the viscosity ratio (viscosity of oil phase/viscosity of water phase) is an important factor for the homogenization efficiency [25]. The reduction of the surfactant molecules available by 50 % (reduced emulsifier concentration) does not lead to a remarkable deviation in the droplet sizes compared to the reference emulsion. Nevertheless, since the reduced emulsifier content might result in a thinner layer on the interface of oil droplets, the droplets could be more sensitive to chemo-physical deterioration during ageing.

#### 3.2 Comparison of the ASLTs impact on the deterioration

The results in figure 4 illustrate that the accelerating storage conditions have both, different effects on the deterioration rate corresponding to the normalized turbidity decay and an effect on the extent of the deterioration. The turbidity drop levels off une-

**Table 3** Parameters of the fitted deterioration functions for the beverages with the four emulsions and the therefrom derived accelerating factors *a*. Bold values of  $\tau^*$  are the ones that are the closest to the value at standard conditions (20 °C), bold values of *a* are the highest identified accelerating factors for each emulsion

Emulsion	Storage condition	$\tau^*$ [-]	$\tau'$ [-]	<i>k</i> [1/d]	<i>a</i> [-]	R <sup>2</sup> [-]
Reference emulsion	40 °C + dark	0.5580	0.4999	0.1939	<b>9.1</b>	0.98789
	40 °C + 5000 Lx	<b>0.5339</b>	0.5229	0.1696	7.9	0.99274
	20 °C + agitation	0.6142	0.4380	0.1755	8.2	0.98877
	20 °C	0.5217	0.4565	0.0214	1	0.99393
Reduced ester gum	40 °C + dark	0.2204	0.7870	0.1436	5.8	0.97048
	40 °C + 5000 Lx	0.2193	0.8192	0.1614	6.5	0.97698
	20 °C + agitation	<b>0.2483</b>	0.8046	0.1923	<b>7.7</b>	0.97306
	20 °C	0.2591	0.6896	0.0249	1	0.99459
Low homogenization pressure	40 °C + dark	0.4667	0.5122	0.1040	9.1	0.96733
	40 °C + 5000 Lx	<b>0.3653</b>	0.6547	0.1099	9.6	0.98942
	20 °C + agitation	0.6085	0.4165	0.1263	<b>11.0</b>	0.98939
	20 °C	0.1908	0.7518	0.0114	1	0.98923
Reduced emulsifier	40 °C + dark	0.5507	0.4937	0.1830	8.7	0.98245
	40 °C + 5000 Lx	<b>0.5127</b>	0.5439	0.1661	7.9	0.99124
	20 °C + agitation	0.5880	0.4582	0.1938	<b>9.2</b>	0.97539
	20 °C	0.4886	0.4494	0.0211	1	0.98274

qually, representing different levels of the kinetically stable state  $\tau^*$ . This effect is particularly identifiable in figure 4 C where the turbidity of the beverage with the weakly homogenized emulsion decreased by over 65 % when illuminated and warmed (40 °C + 5000 Lx) much more as under the other storage conditions. Table 3 condenses the findings by comparing calculated parameters for the fitted decay functions and the resulting accelerating factor *a*.

Among all ASLTs the periodic agitation at 20 °C has the highest deterioration rate for beverages with the product defects-emulsions. Compared to standard conditions (20 °C), periodic agitation accelerates the deterioration by accelerating factors of 7.7 up to 11.0. However, it is noticeable that the minimum level  $\tau^*$  and thus the remaining turbidity respectively shows the highest deviation when agitation is employed. Lifted temperatures (40 °C) accelerate the deterioration by accelerating factor of 5.8 to 9.1. The remaining "stable" cloudiness  $\tau^*$  at warm storage conditions relates close to that at standard conditions as long as the emulsion is not additionally weakly homogenized. This might be of interest for prediction purposes. When adding illuminance to the elevated temperature (40 °C + 5000 Lx) only a minor effect on the accelerating factor is noticed. However, the minimum level  $\tau^*$  here is close to the real-time deterioration under standard conditions.

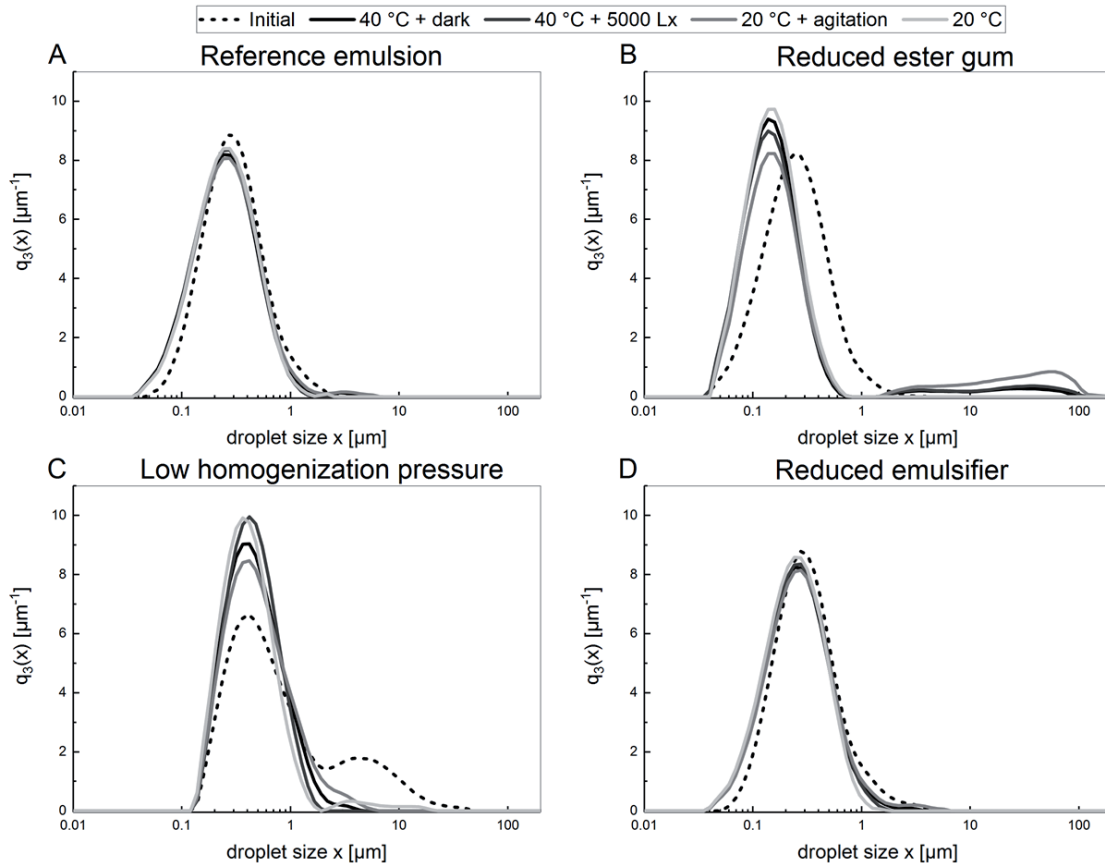
### 3.3 Physical stability of the reference beverage emulsion

The beverage with the reference emulsion is supposed to be sufficiently stable in terms of its physical stability with respect to the requirements in practice. However, changes in turbidity and droplet size distribution were apparent. The turbidity of the beverage samples declined down to 50 % of its initial value. The exposure to elevated temperature conditions and light clearly accelerated the

deterioration process. The turbidity reached an almost constant level from the 25<sup>th</sup> day on (Fig. 4 A). All three ASLTs lead to similar accelerating factors between 7.9 and 9.1 whereas periodic agitation of the beverages results in a slightly higher stable minimum  $\tau^*$  compared to standard conditions.

### 3.4 Emulsion with reduced ester gum concentration

The beverage samples made with the emulsion containing only 2 % weighting agent (ester gum) instead of 6 % in the reference emulsion, show the same rapid drop in turbidity at all accelerating storage conditions in the first 18 days (Fig. 4 B) and reach a very low almost steady minimum down to 20 % of the initial turbidity. At standard conditions the deterioration comes to the same nearly constant level after approximately 100 days. The large turbidity loss is caused by a significant shift in emulsion droplet sizes during storage (Fig. 5 B). The majority of the remaining droplets have diameters of only 30 to 500 nm, whereas a smaller volume fraction is represented by a few larger droplets of 2 to 100  $\mu$ m. As the reduced weighting agent concentration implies a higher amount of partly water soluble substances in the oil phase (orange oil), this emulsion is sensitive to Ostwald ripening. This thermodynamically driven instability phenomenon occurs when the dispersed oil phase shows at least a slight water solubility leading to diffusion of oil molecules from smaller droplets to bigger ones. Normally Ostwald ripening leads to a monomodal droplet size distribution shifting towards higher diameters [26]. One reason for the high span of the droplet sizes of this emulsion could be an incomplete Ostwald ripening process. Since the deterioration comes to a very low constant level, a separation of the enlarged bigger droplets or subsequent disruption of big droplets during laser diffraction measurement is more likely. Nevertheless, the results reveal that all three ASLTs lead to similar deterioration effects in this colloidal



**Fig. 5** Impact of the storage conditions on the droplet size distribution of the four emulsions (A: reference emulsion, B: emulsion with reduced ester gum concentration, C: emulsion homogenized with lower homogenization pressure, D: emulsion with reduced emulsifier concentration) compared to the initial droplet sizes directly after preparation

system. Although Ostwald ripening is a diffusion induced process, agitation is able to enhance this process presumably by reducing diffusion path through continuous mixing.

### 3.5 Insufficiently homogenized emulsion

The intended weak homogenization leads to a bimodal droplet size distribution with a peak at 450 nm and a second one at 4  $\mu\text{m}$  (Fig. 5 C). According to *Piorkowski* and *McClements* an emulsion as this cannot stay stable all along the required shelf-life typical for soft drinks [1]. The results reflect these findings as shown in Figure 4 C. At standard conditions, the beverage lost more than 70 % of its initial turbidity within 180 days. Storing the bottles in the light chamber, the deterioration was accelerated considerably by a factor of about 9 as well as at elevated temperature (40 °C) storage only. Due to a remarkable amount of larger droplets in this beverage emulsion, creaming is a major instability problem for the prepared beverages. Hence, agitation enhances the approximation of the oil droplets and aggregation, accelerating the deterioration remarkably ( $a = 11.0$ ). Nonetheless, creamed droplets can be mixed up again into the beverage matrix resulting in a substantially higher stable minimum of the turbidity  $\tau^*$  compared to non-agitated beverages.

### 3.6 Reduced emulsifier concentration

The changes in turbidity (Fig. 4 D) and initial droplet size distribution (Fig. 5 D) of the beverages with the emulsion having a reduced emulsifier concentration were equivalent to that with the

reference emulsion. Since half of the oil phase consists of highly water insoluble ester gum, Ostwald ripening is negligible even though the interfacial layer is mechanically less strong due to lower surfactant concentration. As discussed previously, steric hindrance is the main stabilization form of OSA starch which is considered to be sufficient even at lower concentrations [14, 21]. Thus, the results show that this weighted orange oil emulsion is stable with respect to the requirements in practice also with only half of the recommend surfactant concentration.

## 4 Conclusion

The examined modified extrinsic factors elevated temperature, enhanced illuminance and periodic agitation as well as combinations of them are capable of accelerating the physical deterioration of weighted orange oil emulsion based soft drinks. Accelerating factors of 5.8 up to 11.0 were achieved. Surprisingly, the periodic agitation without higher temperature or illuminance reveal the highest acceleration factors for all beverages with emulsion defects. Apparently, the collision of droplets and the acceleration of mass transfer (Oswald ripening) play a dominant role for the turbidity loss. This result corresponds to the exponential decline of turbidity in according to a first order law that can be derived from a stochastic collision approach. However, the complex interaction of extrinsic and intrinsic factors could not entirely revealed without an immense experimental set up. Chemical interactions might also have an influence, particularly in OSA-starch stabilized emulsions

[27] and should be considered in further investigations. The effect of light might as well be due to oxidative reactions of oil compounds such as terpenes resulting in changes of viscosity and light absorption. It is thus obvious that the results cannot be transferred to other emulsion formulations like non-weighted cloud emulsions. Nevertheless, for practical purposes the results of the presented work can serve as a basis for the development and assessment of accelerated shelf-life tests. Therefore, not only the accelerating factor but also the extent of the deterioration must be considered. Here unfortunately, the agitation of the beverages without further enhancements – as great it is in accelerating and easy application – exhibits the largest deviation to real-time storage condition. Considering all intrinsic deficiencies of the emulsion beverages, the warm storage with additional illuminance shows the deterioration most similar to the real-time storage. Since the differences in time are not extreme this test condition reveals as most promising.

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