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INFLUENCE OF SELECTED ADDITIVES ON COLLOID STABILITY OF ALCOHOLIC EMULSION CREAMS

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Alcoholic emulsion creams produced using hen's egg yolks (Advocaats) are dense, sweet liqueurs that are characterised by specific sensoric traits satisfying a wide spectrum of consumers. Despite long tradition of liqueur production, the technology in use does not ensure their full uniformity, nor stability during long-term storage. The destabilization rate is determined by many factors, *e.g.* homogenization technique, temperature, aeration as well as the quantitative and qualitative composition of a solution.

We demonstrated that enrichment of the creams with lecithin (0.3%) or sodium caseinate (0.2%) enabled the "full" five-month storage stability. Sodium caseinate addition caused a significant reduction in fat droplets size measured directly after homogenization, but did not inhibit the formation of larger agglomerates *via* droplets joining. It also resulted in the cream's viscosity increase. Advocaats containing elevated lecithin rates were characterised by high resistance to coalescence regardless of the fact that their viscosity was similar to the control samples. Furthermore, the synergistic effect of lecithin and sodium caseinate on storage durability of alcoholic emulsion creams was observed. Samples enriched with both compounds simultaneously, were stable over the five-month storage period, with their lipid phase being more dispersed and the coalescence being slower than in the control. The dispersion to size below 20 μm prolonged the durability of the tested emulsions to a significant extent. The combined application of lecithin (0.1%) and sodium caseinate (0.1%) employed to improve cream stability during storage proved to be efficient in industrial scale samples. Moreover, it was found that pressure homogenization under industrial conditions caused higher (by about 20%) dispersion of lipid fraction in reference to a high-rotation laboratory homogenizer.

INTRODUCTION

Alcoholic emulsion cream is sweet semi-liquid vodka that contains over 400 g/L of total extract and up to 25% vol. of alcohol. Such product as Irish Baileys and Carolans, Scotch Heather (made with the use of whisky), French chocolate-rum Caprice, Dutch Bols, Italian and Czech liqueurs as well as Polish egg-vanilla Advocaat also belong to that group [Nowicki, 1997]. Polish tradition of creams making reaches back to the 16th century and its production technology is still being modified and improved.

Hen's egg yolks that contain about 33% of fat are the main raw material for egg liqueurs production in the alcoholic industry. Disturbance of a very stable physicochemical balance of egg yolk emulsion occurs together with subsequent beginning of fat droplets agglomeration during Advocaat preparation consisting mainly in component mixing under specific conditions. Emulsion stability also changes during storage, due to various physical and chemical factors. The main reason for emulsion instability is the enlargement of lipid phase droplets, associated with flocculation, Ostwald's maturation, coalescence and fat droplets migration which, in turns, leads to cream-formation or sedimentation [McClements, 1999].

Despite of applying modern homogenizing devices (pressure homogenizers), which greatly elevate the emulsion dispersion level, producers fail to achieve a full stability of emulsions during long time storage. Modifications of Advocaat's composition have so far been mainly associated with the addition of plant-originated (lemon or orange juice, ethanol extract of rosemary) [Anduła, 1996] or protein-based agents (powdered milk, hen's albumen) [Żelazny, 1996]. However, the applied additives did not ensure an efficient storage durability of the creams. In order to prolong the colloidal stability, it is recommended to enrich Advocaats with substances reducing their destabilization. Coalescence, leading to cream-formation, may be delayed by application of emulsifiers, *e.g.* lecithin or Tween 20 [Dickinson, 1992; Christov, 2002]. In our earlier studies it was revealed that elevation of lecithin concentration by about 30% contributed to an increase of cream storage durability by 6 months [Tarko & Tuszyński, 2002]. Lecithin content ranged from 1.13 to 1.75 g/100 g in original commercial products of that group. Substances increasing the medium viscosity (sodium caseinate, modified starch, xanthane) are another group of additives that make the particle migration difficult.

The aim of the study was to evaluate the influence of selected stabilizers on storage durability, fat droplets size and viscosity of alcoholic emulsion creams.

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MATERIAL AND METHODS

In order to prepare Advocaat, the following components were used: commercial spirit (96.5% vol.), hen's egg yolks purchased from Agricultural Farm in Goleszów, wine distillate (66.4% vol.) and vanilla ethanol extract (56.1% vol., extract content 13 g/L). The procedure for laboratory preparation of cream (control samples): alcoholic-sugar mixture (58.2 mL of spirit, 2.8 mL of wine distillate, 7.8 mL of vanilla extract, and 106.7 mL of syrup) was added into 55 mL of hen's egg yolks during homogenization (22 000 rpm, 10 min, UltraTurrax T-25 basic homogenizer) and adjusted to 250 mL of total volume.

Laboratory sets of emulsions (250 mL) with stabilizers addition are presented in Table 1 (Stage 1 of experiment). Water solutions of the following stabilizers were prepared as follows: xanthane, sodium caseinate (C.E. Roeper Polska, Swarzędz), oxidized starch (ZETPEZET Piła), low-methylated pectin (made of citrus fruits, 9.5% of methoxy groups) with Mg^{2+} ions as well as β-cyclodextrin (Sigma), then yolk mixture was added, and preliminarily stirred (laboratory stirrer, 150 rpm, 2 min). Subsequently, sets were homogenized by adding all syrup (1000 g/L of extract), spirit, wine distillate and a vanilla ethanol extract. Ethanol solutions of hen-egg-yolk-lecithin and Tween 20 (Sigma) were prepared before homogenization of samples No. 3 and 6 (Table 1). Subsequent procedure was analogous as for previously described sets, but replacing the spirit with earlier prepared stabilizer ethanol solutions (96.5% vol.).

TABLE 1. Addition of stabilizers to the cream samples tested.

Stabilizer type	Concentration in emulsion (% m/V)
Sodium caseinate	0.20 and 0.50
Xanthan	0.05 and 0.10
Lecithin	0.20 and 0.30
Pectin with 3 mmol/L Mg^{2+}	0.05 and 0.10
Oxidized starch (E 1404)	0.50 and 1.00
Tween 20	0.08 and 0.10
β-Cyclodextrin	0.20 and 0.50
Control sample	without additives

Emulsion creams were stored (6 months, ambient temperature, daylight) and subjected to periodical evaluation to test the following traits: (1) *Outer changes* were evaluated by observing the breakings in lower and upper bottle parts and internal breaks as well as visual determination of changes in visible cream structure influencing consumer's interest. (2) *Diameter of fat droplets* – 3 drops of dye (Sudan III) were added into 1 mL of cream and after thorough stirring (20 s) one drop of the solution was placed in Büerker's chamber. Measurements of fat droplets diameter were made using a light microscope (Nikon Eclipse E 600) equipped with Lucia Measurement 4.60 software. At least 150 fat droplets in 3 or 4 different visible zones (magnification 100×) were measured in each sample. Fat dispersion "D" was presented as a ratio of the percentage of droplets smaller than 10 μm (d <10 μm) to those larger than 40 μm (d > 40 μm). (3) *Dynamic viscosity* – determinations were made using Hoeppler's viscosimeter at 20°C and viscosity η was calculated (mPa·s) according to formula: $\eta = K\tau(\delta_k - \delta_c)$; where: K – constant for a sphere; τ – time for sphere falling; δ_k, δ_c – specific weight of sphere and cream, respectively. (4) *Conductance* – the measurement electrode of a conductometer (MultiLab 540) was introduced into the cream (20°C) and result (μS/cm) was read after 5 min.

Setting the creams under laboratory (UltraTurrax T-25 basic homogenizer, 22 000 rpm, 10 min) and industrial conditions (Silesian Plant of Flavoured Vodkas in Bielsko-Biała, pressure homogenizer Alfa-Laval SHL 15, 140 bar) with the addition of two or three stabilizers (Table 2) selected during the 1st stage of the experiment, was subsequently studied phase. The emulsions achieved were evaluated in terms of visual changes, fat droplets size and viscosity during long-term storage.

Results were interpreted after calculating the mean values, standard deviations and confidence intersections ($p<0.05$) from ANOVA test using Instat 3 software.

RESULTS

Influence of storage time on emulsion visual changes

Fat droplets were recorded just after short storage (22 days) in the upper part of the solution supplemented with pectin and magnesium ions, Tween 20 and oxidized starch (1%). The control sample and Advocaat with lecithin addition (0.2%) became destabilized after 38 days. Emulsions enriched with lecithin (0.3%), xanthane, sodium caseinate, oxidized starch (0.5%) and β-cyclodextrin (0.2 and 0.5%) were characterised by high stability (above 100 days).

Creams supplemented with lecithin (0.3%), xanthane (0.1%), Tween 20 (0.08%), sodium caseinate (0.2%) or oxidized starch (0.5%) had no internal nonuniformity. Relatively large internal breakings (from 3 to 5 "cracks" in a bottle of 0.25 mL capacity) were observed in Advocaat with pectin and Mg^{2+} ions.

Addition of xanthane (0.1%) and pectin (0.05 and 0.1%) with magnesium ions into the creams caused separation of clear water-alcoholic layer (about 1 mm) in the lower part of the bottle just in the first month of the experiment. Further storage (118–136 days) elevated instability at bottle's bottom (from 1.5 to 3.5 mm). Advocaats enriched with leci-

TABLE 2. Addition of stabilizers to the cream samples tested.

Stabilizer type	Concentration in emulsion (% m/V)
Control sample	without additives
Tocopherol+lecithin	0.05 + 0.125
Tocopherol+ sodium caseinate	0.05 + 0.1
Lecithin+sodium caseinate	0.125 + 0.1
Sodium caseinate+lecithin+tocopherol	0.1 + 0.125 + 0.05
Control sample[1]	without additives
Lecithin+sodium caseinate[1]	0.1 + 0.1
Lecithin+tocopherol[1]	0.1 + 0.1
Lecithin+sodium caseinate+tocopherol[1]	0.1 + 0.1 + 0.1

[1] – samples set-up in industrial conditions

thin (0.2 and 0.3%) as well as lower concentrations of starch (0.5%) or sodium caseinate (0.2%) did not break and did not produce a water-alcoholic layer even for 136 days.

Creams supplemented with stabilizer mixtures (Table 2) were stable during 122 days of storage, except from samples enriched with lecithin and tocopherol, in which separation of water-alcoholic layer (2 mm) at the bottle's bottom and single fat droplets on the liquid's surface (cream-forming) were found just after two months of storage. First fat droplets on control emulsion's surface were observed just after 2 weeks of storage.

Samples of industrial creams (pressure homogenization) with no stabilizer addition, showed instability symptoms on the 76th day after setting – single fat droplets on liquid's surface and visible water-alcoholic layer (about 1 mm) at bottle's bottom. Durability of Advocaats that contained the combination of three stabilizers (lecithin, sodium caseinate and tocopherol) was prolonged to over 100 days. Their further storage (up to 140 days) did not have any significant influence on destabilization rate.

Influence of storage time on lipid droplets diameter

Directly after setting, the fat droplets size did not exceed 70 μm both in the control sample and emulsions with single stabilizer addition. Maximum dispersion was found in Advocaats enriched with sodium caseinate (0.5%) and β-cyclodextrin (0.2%), where there were over 80% of fat droplets with less than 20 μm in diameter. Creams containing Tween 20 and pectin at 0.1% concentration were characterised by relatively large lipid droplets (about 15% droplets more than 40 μm).

Enlargement of fat droplets in all tested samples occurred during the storage. Creams stabilized with substances increasing the viscosity (xanthane, oxidized starch) were distinguished by their slow growth. Creams with lecithin addition were characterised by the slowest agglomeration of small (< 20 μm) fat droplets into larger ones (> 40 μm).

The fat dispersion D (Figure 1 and 2) in creams with various additives during storage (138 days) was expressed as a ratio of the percentage of droplets with diameter smaller than 10 μm (d < 10 μm) to those larger than 40 μm (d > 40 μm).

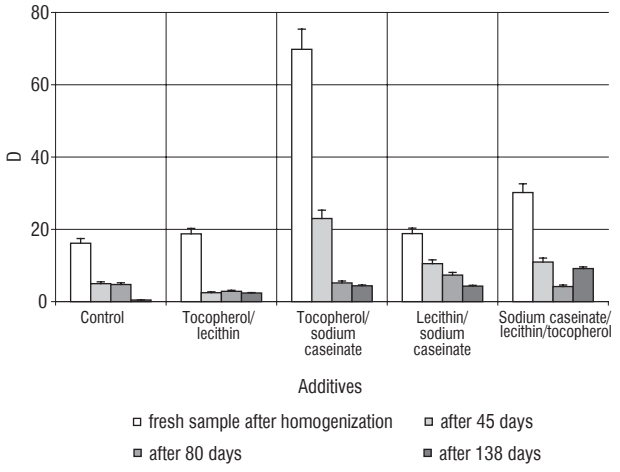

FIGURE 1. Storage time influence on diameter changes in lipid droplets in creams supplemented with stabilizing additives.

$$D = \frac{\text{droplet with diameter} < 10\ \mu m}{\text{droplet with diameter} > 40\ \mu m}$$

Introduction of stabilizing mixtures into the creams (tocopherol and sodium caseinate or sodium caseinate with lecithin and tocopherol), contributed to higher dispersion of fat droplets directly after homogenization (D equals to 70 and 50, respectively). A maximum reduction of coalescence during the storage (by 77% in relation to control) was found in creams enriched with lecithin plus sodium caseinate (Figure 1).

Advocaats set under industrial conditions (pressure homogenizer) showed significantly higher dispersion level (D = 30-60) as compared to the laboratory samples (Figure 2). Introduction of lecithin with sodium caseinate into the creams before homogenization mostly reduced the unfavorable coalescence process (D = 6.2 after 140 days of storage) (Figure 2).

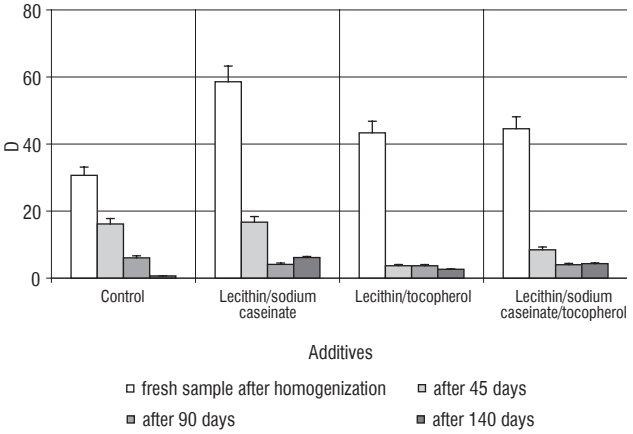

FIGURE 2. Storage time influence on diameter changes in lipid droplets in creams set-up under industrial conditions and supplemented with a mixture of stabilizing additives

$$D = \frac{\text{droplet with diameter} < 10\ \mu m}{\text{droplet with diameter} > 40\ \mu m}$$

Influence of storage time on emulsion viscosity

Viscosity changes of Advocaats enriched with stabilizing additives are presented in Tables 3 and 4. A percentage viscosity increase of each sample calculated in relation to the control just after setting, in further discussion will be referred to as "viscosity index". Oxidized starch (1%) and low-methylated pectin (0.1%) with magnesium ions introduced into the emulsions caused the increase of their viscosity (from 75% to 84%) in relation to the control sample (Table 3). However, the highest increase of the parameter tested (219%) was found after the addition of 0.1% xanthane into the creams. Samples with starch, pectin and xanthane addition were shown to have great viscosity increase during long-term storage (from 85% to 139%) in relation to initial values (Table 3). Advocaats enriched with lecithin, Tween 20 and β-cyclodextrin were distinguished by a much lower viscosity change (9–47%) in reference to the control sample.

Viscosity of creams supplemented with stabilizer mixture was higher in samples containing sodium caseinate (about 130 mPas) as compared to other emulsions (85–109 mPas). The quickest viscosity increase (by about 22% during 119-day storage) was observed in creams containing sodium caseinate. Similar changes of the parameter were noted in Advocaats set under industrial conditions – 55% viscosity increase after 138 days of storage in reference to the control (Table 4).

TABLE 3. Viscosity changes of emulsion samples supplemented with different additives during storage.

Specification	Storage period (days)						Viscosity index* (%)	Change during storage (%)
	1	35	59	90	118	145		
	Viscosity (mPa·s) ± SD							
Control	74.6 ± 3.73	70.0 ± 3.50	73.7 ± 3.69	94.1 ± 4.71^{b}	86.2 ± 4.31	87.6 ± 4.50	—	17
Oxidized starch 0.5%	109.8 ± 5.49^{a}	168.1 ± 8.41^{a,b}	182.0 ± 9.10^{a,b}	197.8 ± 9.89^{a,b}	204.7 ± 10.24^{a,b}	262.6 ± 13.13^{a,b}	47	139
Oxidized starch 1%	137.5 ± 6.88^{a}	203.3 ± 10.17^{a,b}	189.3 ± 9.47^{a,b}	209.0 ± 10.45^{a,b}	211.6 ± 10.58^{a,b}	297.1 ± 14.89^{a,b}	84	116
Xanthan 0.05%	104.2 ± 5.21^{a}	124.6 ± 6.23^{a,b}	161.1 ± 8.06^{a,b}	210.7 ± 10.54^{a,b}	199.6 ± 9.98^{a,b}	246.3 ± 12.32^{a,b}	40	136
Xanthan 0.1%	238.1±11.9^{a}	251.7 ± 12.59^{a}	369.0 ± 18.45^{a,b}	490.6 ± 24.54^{a,b}	466.4 ± 23.32^{a,b}	537.1 ± 26.70^{a,b}	219	125
Tween 0.08%	95.5 ± 4.78^{a}	100.5 ± 5.03^{a}	101.9 ± 5.10^{a}	123.3 ± 6.17^{a,b}	125.6 ± 6.28^{a,b}	137.6 ± 6.88^{a,b}	28	44
Tween 0.1%	81.5 ± 4.08	100.6 ± 5.11^{a,b}	99.6 ± 4.98^{a,b}	144.1 ± 7.21^{a,b}	132.0 ± 6.60^{a,b}	177.8 ± 8.88^{a,b}	9	118
Sodium caseinate 0.2%	101.9 ± 5.10^{a}	128.2 ± 6.41^{a,b}	120.4 ± 6.02^{a,b}	140.8 ± 7.04^{a,b}	135.3 ± 6.77^{a,b}	156.5 ± 7.83^{a,b}	37	53
Sodium caseinate 0.5%	109.3 ± 5.47^{a}	148.2 ± 7.41^{a,b}	186.1 ± 9.31^{a,b}	227.4 ± 11.37^{a,b}	216.3 ± 10.72^{a,b}	211.2 ± 10.56^{a,b}	47	93
β-Cyclodextrin 0.2%	88.4 ± 4.42^{a}	121.8 ± 6.09^{a,b}	101.4 ± 5.07^{a,b}	107.9 ± 5.40^{a,b}	115.8 ± 5.79^{a,b}	118.1 ± 5.92^{a,b}	18	33
β-Cyclodextrin 0.5%	82.9 ± 4.15	109.3 ± 5.47^{a,b}	100.9 ± 5.05^{a,b}	123.2 ± 6.16^{a,b}	124.6 ± 6.23^{a,b}	127.0 ± 6.39^{a,b}	11	53
Lecithin 0.2%	109.3 ± 5.47^{a}	132.0 ± 6.60^{a,b}	117.7 ± 5.89^{a}	121.9 ± 6.10^{a}	123.3 ± 6.17^{a,b}	120.0 ± 6.00^{a}	47	10
Lecithin 0.3%	100.1 ± 5.01^{a}	124.6 ± 6.23^{a,b}	115.8 ± 5.79^{a,b}	126.5 ± 6.33^{a,b}	126.5 ± 6.33^{a,b}	129.7 ± 7.52^{a,b}	34	30
Pectin 0.05% + Mg^{2+}	115.4 ± 5.77^{a}	176.6 ± 8.83^{a,b}	196.8 ± 9.84^{a,b}	227.0 ± 11.35^{a,b}	220.2 ± 11.01^{a,b}	217.1 ± 10.86^{a,b}	55	88
Pectin 0.1% + Mg^{2+}	130.8 ± 6.54^{a}	209.4 ± 10.47^{a,b}	209.4 ± 10.12^{a,b}	232.5 ± 11.63^{a,b}	242.8 ± 12.14^{a,b}	242.2 ± 12.11^{a,b}	75	85

* viscosity increase in relation to control sample, just after setting-up; [a] statistically significant in comparison to control ($p < 0.05$); [b] statistically significant as compared to t=1 day ($p < 0.05$)

TABLE 4. Viscosity changes of cream supplemented with different set off stabilizers during storage.

Specification	Storage period (days)					Viscosity index * (%)	Change during storage (%)
	1	42	63	89	119		
	Viscosity (mPa·s) ± SD						
Control	91.6 ± 4.58	93.3 ± 5.60^{b}	96.1 ± 6.72^{b}	99.2 ± 6.94^{b}	100.2 ± 5.51^{b}	—	9
Tocopherol/lecithin	109.3 ± 5.47^{a}	112.4 ± 6.74^{a,b}	115.9 ± 8.11^{a,b}	116.2 ± 8.13^{a,b}	120.7 ± 6.64^{a,b}	19	10
Tocopherol/sodium caseinate	120.2 ± 6.01^{a}	125.6 ± 7.54^{a,b}	129.1 ± 9.04^{a,b}	136.8 ± 9.58^{a,b}	138.9 ± 7.64^{a,b}	31	16
Lecithin/sodium caseinate	135.7 ± 6.79^{a}	149.2 ± 8.95^{a,b}	153.1 ± 10.72^{a,b}	161.1 ± 11.28^{a,b}	169.4 ± 9.32^{a,b}	48	25
Sodium caseinate/lecithin/tocopherol	138.1 ± 6.91^{a}	145.2 ± 8.71^{a,b}	160.7 ± 11.25^{a,b}	167.1 ± 11.70^{a,b}	171.7 ± 9.44^{a,b}	51	24
	1	40	78	114	138		
Control[1]	85.2 ± 4.26	91.2 ± 5.47^{b}	93.4 ± 6.54^{b}	95.1 ± 6.66^{b}	99.2 ± 5.46^{b}	—	16
Lecithin/sodium caseinate[1]	129.7 ± 6.49^{a}	134.1 ± 8.05^{a,b}	145.2 ± 10.16^{a,b}	152.4 ± 10.67^{a,b}	158.8 ± 8.76^{a,b}	52	22
Lecithin/tocopherol[1]	101.7 ± 5.09^{a}	108.1 ± 6.49^{a,b}	112.3 ± 7.89^{a,b}	114.9 ± 8.05^{a,b}	118.8 ± 6.53^{a,b}	19	17
Lecithin/sodium caseinate/tocopherol[1]	132.3 ± 6.62^{a}	138.7 ± 8.02^{a,b}	151.3 ± 10.59^{a,b}	159.9 ± 11.19^{a,b}	162.8 ± 8.95^{a,b}	55	23

[1] samples set-up in industrial conditions; * viscosity increase in relation to control sample, just after setting-up; [a] statistically significant in comparison to control ($p < 0.05$); [b] statistically significant as compared to t = 1 day ($p < 0.05$)

Influence of storage time on emulsion conductance

Results presented in Table 5 indicate that the decrease of the conductance occurred during the storage. Creams with 0.1% Tween 20 and 0.5% of oxidized starch addition were characterised by the strongest conductance decrease (from 25% to 27%) in relation to the initial value. The control samples as well as Advocaats enriched with lecithin (0.2% and 0.3%) did not show any significant conductance changes during five months – only by 6%, on average.

There was no correlation between emulsion conductance and droplet size in dispersed phase. Samples of Advocaats with the addition of 0.5% of β-cyclodextrin containing a high percentage of droplets with diameter below 20 μm usually showed a small conductance decrease (about 8%). It is important that creams enriched with oxidized starch be characterised by the largest conductance decrease during the storage (from 99 to 72 μS/cm), despite relatively great share of small fat droplets (Table 5).

DISCUSSION

The study performed revealed that the durability of Advocaats depended on the supplements applied. Lecithin naturally occurring in hen's egg yolks is a basic component that stabilizes creams, but its level is insufficient to achieve a proper storage durability, namely in Advocaats with high density and alcohol content above 20% vol. Experiments performed revealed that the addition of 0.3 g lecithin per 100 mL

TABLE 5. Conductivity changes of tested samples during storage.

Specification	Storage period (days)						Change during storage (%)
	1	35	59	90	118	145	
	Conductivity (μS/cm) ± SD						
Control	110.3 ± 2.21	112.4 ± 3.37	115.7 ± 1.26[b]	109.2 ± 2.18	108.8 ± 3.23	112.5 ± 1.13[b]	2
Oxidized starch 0.5%	99.1 ± 1.98[a]	93.6 ± 2.81[a,b]	88.2 ± 0.98[a,b]	84.5 ± 1.69[a,b]	82.7 ± 2.48[a,b]	72.5 ± 0.73[a,b]	27
Oxidized starch 1%	109.9 ± 2.20	95.9 ± 2.88[a,b]	95.7 ± 1.02[a,b]	88.9 ± 1.73[a,b]	92.8 ± 1.87[a,b]	82.5 ± 0.97[a,b]	25
Xanthan 0.05%	111.8 ± 2.24	114.3 ± 3.43[a,b]	101.5 ± 1.06[a,b]	89.2 ± 1.78[a,b]	86.6 ± 2.60[a,b]	87.4 ± 1.01[a,b]	22
Xanthan 0.1%	108.3 ± 2.17[a]	108.6 ± 3.26[a]	95.2 ± 0.95[a,b]	87.8 ± 1.76[a,b]	85.5 ± 2.76[a,b]	87.5 ± 3.24[a,b]	19
Tween 0.08%	112.1 ± 2.32[a]	108.8 ± 3.21	110.0 ± 1.10[a,b]	101.0 ± 2.02[a,b]	99.9 ± 3.00[a,b]	96.6 ± 1.23[a,b]	14
Tween 0.1%	112.4 ± 2.25[a]	112.1 ± 3.36[a,b]	108.8 ± 1.09[a,b]	98.8 ± 1.91[a,b]	97.0 ± 2.91[a,b]	82.2 ± 2.15[a,b]	27
Sodium caseinate 0.2%	96.8 ± 1.94[a]	93.8 ± 2.81[a,b]	94.2 ± 1.52[a,b]	88.2 ± 1.77[a,b]	88.1 ± 2.34[a,b]	84.2 ± 1.14[a,b]	13
Sodium caseinate 0.5%	88.0 ± 1.76[a]	91.2 ± 2.74[a,b]	78.9 ± 1.11[a,b]	74.1 ± 1.48[a,b]	74.5 ± 2.64[a,b]	76.8 ± 1.68[a,b]	13
β-Cyclodextrin 0.2%	105.8 ± 2.12[a]	95.5 ± 2.78[a,b]	103.8 ± 2.03[a,b]	101.5 ± 2.03[a,b]	97.4 ± 2.92[a,b]	97.3 ± 2.01[a,b]	8
β- Cyclodextrin 0.5%	97.0 ± 1.96[a]	94.5 ± 2.84[a,b]	99.9 ± 0.79[a,b]	92.1 ± 1.84[a,b]	92.0 ± 2.76[a,b]	89.4 ± 1.56[a,b]	8
Lecithin 0.2%	103.2 ± 2.06[a]	102.9 ± 3.09[a]	108.3 ± 1.04[a]	107.2 ± 2.14[a]	104.0 ± 3.12[a]	107.3 ± 2.59[a,b]	4
Lecithin 0.3%	105.5 ± 2.00[a]	108.2 ± 3.25[a,b]	106.5 ± 1.00[a]	102.5 ± 2.05[a,b]	102.2 ± 3.16[a,b]	103.9 ± 2.99[a]	2
Pectin 0.05% + Mg^{2+}	134.8 ± 2.70[a]	122.3 ± 3.67[a,b]	121.3 ± 1.21[a,b]	107.2 ± 2.10[a,b]	105.2 ± 3.07[a,b]	110.4 ± 2.41[a,b]	18
Pectin 0.1% + Mg^{2+}	126.3 ± 2.53[a]	117.9 ± 3.54[a,b]	112.9 ± 1.13[a,b]	109.2 ± 1.79[b]	104.4 ± 3.13[a,b]	108.5 ± 1.97[a,b]	14

[a] statistically significant in comparison to control ($p < 0.05$); [b] statistically significant as compared to t = 1 day ($p < 0.05$)

of Advocaat ensured its physical stability during long-term storage (145 days), in spite of the increase in the number of fat droplets over 40 μm in diameter. Anduła [1996] and Żelazny [1996] achieved similar prolongation of the storage durability in experiments with lecithin.

The dispersion level of fresh creams supplemented with lecithin (0.3%) and control samples was similar, but the applied stabilizer significantly reduced the coalescence. Bylaite *et al.* [2001] and Tirok *et al.* [2001] prepared emulsion containing sunflower oil and applied lecithin as a stabilizer, which resulted in an almost two-fold reduction of fat droplets aggregation in larger groups during 8 days of observation. The coalescence phenomenon in model samples depends first of all on surfactants applied and homogenization manner, whereas the durability of Advocaats is moreover determined by density and viscosity of a medium as well as alcohol concentration.

When analysing the influence of stabilizers applied in the reported experiments on the emulsion viscosity, it is apparent that lecithin (0.2%) contributed to its increase (Table 3). An earlier study of Nielepkowicz-Charczuk *et al.* [1996] revealed that viscosity increased by about 14% over 4-month storage of similar samples of Advocaats. Therefore, lecithin can be considered as a good stabilizer of emulsion creams that improves the stability of Advocaats when applied at relatively low concentrations, and slight viscosity change does not negatively affect the bottle emptying yet.

Sodium caseinate at 0.2% concentration was also the substance determining the suitable durability of Advocaats during long-term storage. Medium-molecular proteins positively influence the formation of small-particle emulsions with high surface tension. They also intensify the electrostatic interactions between droplets, which contributes to their strong dispersion [Dickinson, 1992; Schokker & Dalgleish, 1998]. Burgaud & Dickinson [1990] found that sodium caseinate addition (0.25%) into the alcoholic emulsion (0–40% vol.) affected positively its stability. However, higher doses of the emulsifier (0.5%) applied in the present experiments, contributed to the deterioration of the tested Advocaats durability. Furthermore, higher concentrations of sodium caseinate may lead to the formation of water-alcoholic layer through emulsion salting out. Sodium caseinate in water solutions dissociates and sodium cations formed determine negative changes in the structure [McClements, 1999].

Adding the sodium caseinate into the fresh Advocaats caused a decrease in fat droplets size as compared to the control creams. However, they grew again during their storage for a longer time. Therefore, it should be expected that those changes may accelerate the cream-forming process producing the fat ring on a liquid surface. Sodium caseinate at 0.2% concentration, due to great water absorption capacity, causes viscosity increase and reduction of Brown's movements [Muir & Dalgleish, 1987]. Thus, it can be supposed that this property of sodium caseinate protected the emulsion against the oil layer formation on the surface.

High water absorption capacity of sodium caseinate was also the reason for over two-fold viscosity increase in the samples tested (Table 3), but only 0.5% concentration unfavorably decreased their liquidity. Earlier study of Muir & Dalgleish [1987] as well as Dickinson & Golding [1997] indicated that the addition of sodium caseinate into some emulsions caused even three-fold viscosity increase, but the tested samples were characterised by much lower initial viscosity (about 10 times) as compared to creams in our own tests.

Oxidized starch (0.5%) was another component that ensured the stability of Advocaat samples during 145 days of storage. According to McClements [1999], starch addition into the emulsion decreased the mobility of dispersed phase droplets, which protected it against coalescence and cream-formation. However, the addition of oxidized starch at the concentration of 0.5% caused a significant (over three-fold) viscosity increase of the creams analysed (Table 3), which made it difficult to empty the bottle.

A combined addition of lecithin and sodium caseinate (Table 2) is worth of particular interest. Their supplementation at the amount of 0.1% (lower concentration as in the case of single components) ensured full storage durability of emulsion during the tested period (120 days), which may suggest additive or synergistic effect.

The size of fat droplets of the emulsions tested significantly depended on the applied stabilizer type (Figure 1). The addition of lecithin plus sodium caseinate or lecithin, sodium caseinate plus tocopherol contributed to the improvement of homogenization effect – about 70% of fat droplets with less than 20 μm in diameter. Both lecithin and sodium caseinate are in the group of compounds stabilizing the O/W type emulsion, but they are distinguished by different mechanisms that fix multi-phase systems. Lecithin is oriented with its hydrophilic and lypophilic groups towards water and lipid phase, respectively, which protects against agglomeration of droplets formed during homogenization process [Courthaudon & Dickinson, 1997; van Aken 2002]. Protein stabilizers (sodium caseinate) form cross-linked structures separating fat droplets from one another and reducing their collisions due to chaotic Brown's movements [Dalgleish *et al.,* 1997]. Moreover, sodium caseinate causes the increase of medium viscosity, which results in the reduction of Brown's movements and delays coalescence.

An analysis of results presented in Table 4 indicates that sodium caseinate that is characterized by strong water absorption [Dalgleish *et al.* 1997] and ability to form cross-linked structures [Casanowa & Dickinson, 1998], contributes to the increase of dynamic viscosity of the creams tested.

A statistically significant decrease of conductivity (from 2% to 27%) (Table 5) was observed in stored emulsions, except from samples with lecithin addition and control solutions. Probable agglomeration of lipid droplets into larger groups exerted a great influence on conductance increase, which led to their amount decrease in a volume unit, thus making ions transfer between electrodes easier. The increase of conductance along with the increase of fat droplets size may be also accounted for by the so-called *double electric layer*: the higher the diameter of fat droplets, the lower the surface where ions can be adsorbed. Part of those ions is transferred into the solution resulting in the increase of its conductance.

It can be supposed from our results that direct conductometric measurements are a not credible test for the evaluation of alcoholic emulsion creams stability. It would be difficult to indicate numerical values determining a given durability of emulsion. Thus, *electric impulse counting* would be an alternative technique for Advocaats evaluation [McClements, 1999].

Setting the Advocaats under industrial conditions served as a summarizing of the study on prolongation of the emulsion creams storage durability and verifying the results of laboratory experiments.

Applying the pressure homogenization (Alfa-Laval SHL 15, 140 bar) contributed to a great reduction in fat droplets in the samples tested (Figure 2) – their diameters were significantly smaller (from 35% to 65%) than in the creams set with the same additives under laboratory conditions. The share of lipid droplets below 20 μm in diameter ranged from 77.8% to 85.2%. It should be mentioned that there is a lack of closer information on ethanol-containing emulsions in literature. Most of works describe experiments using model laboratory emulsions. Linares *et al.* [2001] observed two times higher dispersion of emulsion prepared from oil, water and hexadecanol after pressure homogenization application. Maa & Hsu [1996], in their experiments on O/W type laboratory emulsions set using a high-speed (10 000 rpm) homogenizer, achieved fat droplets with diameters less than 10 μm, and Floury *et al.* [2000] found that the share of lipid phase particles less than 1 μm in diameter was over 90% after pressure homogenization.

Fat droplets were coalescenced forming larger agglomerates during the industrial samples storage. Creams containing lecithin and sodium caseinate were characterised by high stability. The destabilization processes occurred much faster in samples with lecithin addition but without sodium caseinate. The experiments in industrial scale revealed that additive or synergistic effects of both constituents were probable. Therefore, it is beneficial to apply the combined additives to protect emulsion against breaking.

Emulsion creams (with sodium caseinate addition) set under industrial conditions (Table 4) were characterised by statistically significant ($p < 0.05$) higher viscosity as compared to other samples. Similar results were achieved during the evaluation of laboratory emulsions dispersed using a high-speed homogenizer. Creams set in a laboratory were distinguished by higher (by about 6%) viscosity in reference to the industrial samples. The viscosity decrease may have occurred due to higher dispersion of fat droplets during pressure homogenization. In opinion of Floury *et al.* [2000], the dispersion reduces the formation of lipid fraction agglomerates, which decreases the solution viscosity. Industrial samples confirmed the positive influence of sodium caseinate and lecithin as well as the combined action of lecithin, sodium caseinate and tocopherol on the stability of emulsions tested.

CONCLUSIONS

1. The size of fat droplets significantly influences the stability of alcoholic emulsion creams during the storage. Dispersion of about 80% of lipid fraction to the size below 20 μm prolongs the storage durability of the system by about 60 days.

2. An increase of lipid phase dispersion and delay of the coalescence process may be achieved by the addition of lecithin (0.3%) or sodium caseinate (0.2%) into the creams. Simultaneous enrichment of the creams with lecithin (0.1%) and sodium caseinate (0.1%), ensures full physical stability of emulsion during five-month storage.

3. The addition of the substances significantly increasing viscosity (oxidized starch, xanthane, pectin) into alcoholic emulsion creams, does not guarantee their storage stability for a longer period of time (above 60 days). Supplementation of the tested emulsion sets with sodium caseinate (0.2%) contributes to the increase of their initial viscosity by about 50%.

4. Pressure homogenizers ensure better fat phase dispersion under industrial conditions (over 80% droplets with diameter less than 20 μm) in comparison to a laboratory high-speed homogenizers (about 60% droplets with diameter less than 20 μm).

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WPŁYW WYBRANYCH DODATKÓW NA TRWAŁOŚĆ KOLOIDALNĄ ALKOHOLOWYCH KREMÓW EMULSYJNYCH

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Kremy alkoholowe wyprodukowane na bazie żółtek jaj kurzych (Advocaaty) są to gęste, słodkie likiery, charakteryzujące się specyficznymi cechami sensorycznymi, które satysfakcjonują liczną grupę konsumentów. Mimo wieloletniej już tradycji produkcji kremów, stosowane dotychczas technologie nie zapewniają pełnej ich jednorodności i trwałości w czasie długotrwałego przechowywania. Szybkość procesu destabilizacji uwarunkowana jest wieloma czynnikami, między innymi sposobem homogenizacji, temperaturą, natlenieniem oraz składem ilościowym i jakościowym roztworu.

Doświadczenia wykazały, że wzbogacenie kremów lecytyną (0,3%) lub kazeinianem sodu (0,2%) warunkowało pełną trwałość przechowalniczą, w czasie pięciomiesięcznego składowania. Dodatek kazeinianu sodu powodował znaczną redukcję wielkości kropelek tłuszczu bezpośrednio po homogenizacji, jednak nie ograniczał zjawiska ich łączenia się w większe aglomeraty. Użyty stabilizator przyczyniał się również do wzrostu lepkości kremów (tab. 3). Advocaaty zawierające zwiększone dawki lecytyny charakteryzowały się wysoką odpornością na koalescencję pomimo, że ich lepkość była podobna jak w próbach kontrolnych. Wykazano ponadto addytywny efekt oddziaływania lecytyny i kazeinianu sodu na trwałość przechowalniczą alkoholowych kremów emulsyjnych. Próby wzbogacone jednocześnie w obydwa związki były stabilne w czasie pięciu miesięcy składowania (rys. 1). Faza lipidowa emulsji ulegała silniejszemu, w odniesieniu do kontroli, zdyspergowaniu oraz wolniejszej koalescencji. Ich dyspersja do rozmiarów poniżej 20 μm wydłużała w zasadniczy sposób trwałość badanych emulsji. W próbach wykonanych na skalę przemysłową wykazano skuteczność stosowania łącznie kazeinianu sodu (0,1%) oraz lecytyny (0,1%) do poprawy stabilności kremów podczas magazynowania (rys. 2). Stwierdzono ponadto, że homogenizacja ciśnieniowa w warunkach przemysłowych zapewnia wyższe (o około 20%) zdyspergowanie frakcji lipidowej, w odniesieniu do wysokoobrotowego homogenizatora laboratoryjnego.