EFFECT OF OIL PHASE CONCENTRATION ON RHEOLOGICAL PROPERTIES AND STABILITY OF BEVERAGE EMULSIONS

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Abstract. The influence of oil phase concentration on rheological properties and stability of the beverage emulsions with selected hydrocolloids was studied. The emulsions were stabilized by arabic gum, ghatti gum and modified starch. The stability of emulsions was determined by turbidimetric method and laser scattering method. Storage test of emulsions and beverages was carried out for 12 weeks. The apparent viscosity of emulsions was determined. Independently of the kind of used emulsifier the increase of oil concentration in range 20-40% caused increase of apparent viscosity and opacity of emulsions and beverages. In the case of emulsions with ghatti gum no effect of oil concentration on emulsions stability was observed. In the case of emulsions with modified starch small decrease of beverages stability was found. The largest changes were found in emulsions with arabic gum.

Key words: beverage emulsions, stability, viscosity, arabic gum, ghatti gum, modified starch

INTRODUCTION

Beverage emulsions are oil-in-water emulsions. They are prepared as a concentrate, and then diluted in sugar solution in order to produce the finished beverage [Buffo and Reineccius 2000, 2002]. The emulsion in both its concentrated and diluted form must have a high degree of stability [Tan and Holmes 1988, Buffo et al. 2001]. In soft drinks the beverage emulsion may provide flavour, colour and suitable cloudy appearance [Reineccius 1994]. The oil phase of beverage emulsions consists of flavour oils and weighing agents, whereas the aqueous phase consists of dissolved in water: emulsifiers, acids, preservatives, and colourings [Buffo and Reineccius 2000, Chanamai and McClements 2001]. Natural and identical to natural flavouring substances are basic and necessary components of beverage emulsions. The most commonly used flavouring substances are essential oils, mainly citrus oils [Kaufman and Garti 1984]. Citrus oils

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are primarily comprised of hydrocarbon terpenes (monoterpenes and sesquiterpenes) that have little odour or taste themselves. The oxygenated terpenoids, for example, alcohols, ketones, acids, and esters do contribute to the overall flavour profile of citrus oils [Tan 2004].

The purpose of weighing agents is to increase the oil phase density to level of density of continuous phase and following to level of density of sugar solution, thereby reducing the tendency for creaming [Kaufman and Garti 1984, Garti et al. 1991]. Hydrocolloids serve as emulsifiers and stabilizers in beverage emulsions. Hydrocolloids stabilize emulsions through viscosity effects, steric hindrance and electrostatic interactions [Chanamai and McClements 2002]. Hydrocolloids suitable for stabilizing beverage emulsions must have high solubility in cold water, low viscosity in solution, high emulsifying capacity and no thickening and/or gelling effects with aging [Tan and Holmes 1988]. The most widely used hydrocolloids currently in beverage emulsions are amphiphilic polysaccharides such as gum arabic and modified starch [Garti 1999, Turbiano 1995].

Emulsion instability results from physical processes, i.e. flocculation, coalescence, Ostwalda ripening and gravitation separation. The rate of these changes can be measured by determining the size and distribution of oil droplets in the emulsion [McClements and Coupland 1996]. Stokes' law states that the velocity at which a droplet moves is proportional to the square of its radius. The stability of an emulsion to gravitation separation can therefore be enhanced by reducing the size of the droplets [Chanamai and McClements 2000, Huang et al. 2001].

The concentration of oil phase in emulsion plays an important role in determining its appearance, texture, flavour and stability [McClements 2004]. The ratio of emulsifier/oil, which indicates the coverage level of the oil droplets by the emulsifier, has a large influence on emulsion stability [Jacome-Guth et al. 1991].

The aim of this study was to evaluate the effect of oil phase concentration on rheological properties and stability of the beverage emulsions taking into account the kind of hydrocolloids which were used as emulsifiers and stabilizers.

MATERIAL AND METHODS

Valgum (gum arabic I), Valspray (gum arabic II) and Valrosin D (rosin esters) were provided by the Valmar. Modified starch (starch sodium octenyl succinate) – Purity Gum 2000 was obtained from the National Starch and Chemical. Ghatti gum was obtained from Hortimex. Essential oil was purchased from Pollena Aroma. Sodium benzoate and citric acid were obtained from Orffa Food Eastern Europe. Gum arabic I and gum arabic II were mixed in proportion 1:1. In this paper the obtained mixture was called gum arabic.

The emulsions were prepared according to the following formula: oil phase (natural essential oil and rosin esters in proportion 1:1) – 20, 30 or 40% (w/w), emulsifier (gum arabic or modified starch) – 12% (w/w) or emulsifier (gum ghatti) – 3% (w/w), sodium benzoate – 0.1% (w/w), citric acid – 0.3% (w/w), and distilled water up to 100% (w/w).

A fine emulsion was achieved by subjecting the premixes to a two-stage homogenization with an APV-1000 homogenizer produced by APV, at 55 MPa in the first stage and 18 MPa in the second stage.

The beverages were obtained by dissolving in distilled water (1000 g) sugar (50 g) and emulsion (2 g). PH of the beverages was adjusted to 3.5 with 2M citric acid.

Apparent viscosity determination

The apparent viscosity of beverage emulsions was determined with use of Brookfield model RV using spindle SC4-28 at temperature 20 ±2°C. The dependence of viscosity from shear rate was marked by using Rheolac V 1.1 program.

Particle size determination

Mean particle size and particle size distribution of the disperse phase of beverage emulsions were determined with static light scattering using a Malvern Mastersizer (Malvern Instruments Ltd., Malvern, UK) on the next day after preparation. The samples of emulsion were diluted 1 to 200 with distilled water. Each sample was analysed three times, and the data are presented as the average. The average droplet size was characterized by mean diameters related to the volume $D_{[4,3]}$ defined respectively by:

$$D_{[4,3]} = \frac{\sum_i n_i d_i^4}{\sum_i n_i d_i^3} \tag{1}$$

where: n_i – number of droplets of diameter d_i.

Turbidity measurement of emulsion stability

Before the measurement of absorbance each sample of emulsion was diluted in relation 1 to 1000, while the beverages in relation 1 to 2. The absorbance was taken at 400, 660 and 800 nm, using Helios β spectrophotometer (Unicam). From the absorbance values at 660 nm the opacity (O) was determined, and from the ratio of absorbance at 800 and 400 nm the size index (R) was determined [Kaufman and Garti 1984].

The storage test

Samples of emulsion in glass jar type Twist-off as well as soft drinks (PET bottles 1 litre) were stored at least for 12 weeks at temperature 20 ±2°C. The visible ringing or sediment or emulsion breaking indicated instability of emulsion.

Statistical analysis

The statistical analysis was carried out with use of the computer program *Statgraphics Plus Version 5* produced by Statgraphics Plus Corporation, using analysis of variance ANOVA and Multiple – Sample Comparison, at a confidence level of 5%.

RESULTS AND DISCUSSION

The influence of the concentration of disperse phase on stability of beverage emulsions was estimated using the samples with 10, 15 and 20% of essential oil, what corresponds to 20, 30 and 40% of contents of oil phase. Taking into account the fact that this influence can be different depending on the kind of used emulsifier, emulsions were stabilized by gum arabic or modified starch or gum ghatti.

Rheological properties of component phases as well as the emulsion itself have essential influence on emulsion stability [Buffo and Reineccius 2002], so the influence of oil phase concentration on apparent viscosity of emulsion was analysed. The results of determination of apparent viscosity of emulsion are shown in Figure 1. The apparent viscosity is shown as a function of the shear rate. Arabic gum emulsions and ghatti gum emulsions, independently of disperse phase concentration, behaved as non-Newtonian liquids, while emulsion stabilised by modified starch with addition of 20% of oil phase had properties of Newtonian liquid. Its viscosity did not change with increase of the shear rate. The increase of oil phase addition up to 30% and more to 40% caused significant increase of viscosity of all examined emulsions and what is more, the emulsions stabilized by modified starch with addition of 30 and 40% of oil phase revealed the properties of non-Newtonian liquid. The observed increase of viscosity of emulsions with increasing of the concentration of disperse phase corresponds to the literature. The researches of the rheological properties of emulsions showed that one of the most important factor which influences on their viscosity is *the disperse phase volume fraction* ϕ, which is equal to the volume of emulsion droplets divided by the total volume of emulsion [McClements 2004]. In dilute emulsions ($\phi < 0.05$) the dependence of viscosity η to oil phase volume fraction can be described as Einstein equation:

$$\eta = \eta_1\left(1 + 2.5\varphi\right) \tag{2}$$

where: η_1 – the viscosity of the aqueous phase.

The Einstein equation is true for spherical and rigid particles, if no interactions between them appear, there is no slip particle – liquid and motion of particles is unimportant. This equation predicts that viscosity of diluted suspensions of rigid spherical particle increases linearly with particle volume [Tadros 1994, Klinkesorn et al. 2004].

As the concentration of oil phase increases, measured viscosity exceeds this expected from the Einstein equation. It is caused by interactions between disperse phase particles. Hydrodynamic and colloidal interactions change the viscosity of system by increasing the degree of disturbance of normal liquid flow. Many equations which take into account interactions between oil droplets, being the extension of the Einstein equation, are used for the concentration emulsions [Campanella et al. 1995, Chanamai and McClements 2000, Quemada and Berli 2002].

The analysis of data shown in Figure 1 allows to make the statement that the increase of apparent viscosity of beverage emulsions was considerably larger than the expected one from Einstein equation. It proves that there are strong colloidal interactions in emulsions. The occurrence of colloidal interactions (electrostatic and steric) causes that not oil phase volume fraction (counted on the basic of amount of oil addition to emulsion) but considerably larger so-called effective volume fraction influence the emulsion viscosity [Buffo and Reineccius 2002, McClements 2004].
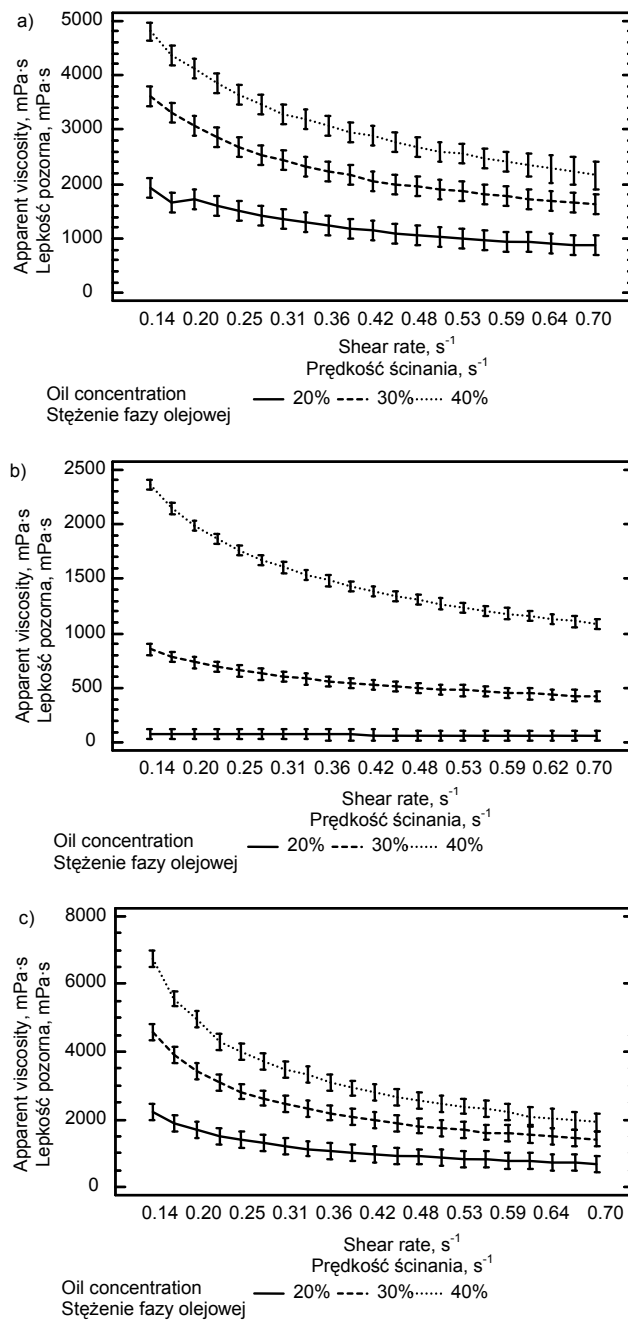
Fig. 1. Apparent viscosity of emulsions stabilized by: a) arabic
gum, b) modified starch, c) ghatti gum
Rys. 1. Lepkość pozorna emulsji stabilizowanych: a) gumą
arabską, b) skrobią modyfikowaną, c) gumą ghatti (I-NIR)

In emulsions with addition of arabic gum the increase of oil phase addition causes clear increase of the average size of oil droplets $D_{[4,3]}$ (Table 1) as well as considerable extension of droplet size distribution (Fig. 2). In emulsions stabilized by arabic gum to which 20% of oil phase was added more than 90% of particles had diameters below 1 μm, but as the oil phase concentration was higher only 48% (for 30% of addition) and 26% (for 40% of addition), respectively. Probably, it was so because the used amount of gum arabic was not enough to cover the surface of oil droplets when the concentration of oil phase was higher. Jacome-Guth et al. [1991], investigating the beverage emulsion stability, found that proportion of gum arabic concentration to oil concentration, that points to the degree of oil droplets coverage by emulsifier, has an influence on emulsion stability. According to authors in order to obtain the stable emulsion, when the degree of oil concentration is known, the ratio of gum arabic amount to oil amount should be as high as possible.

Table 1. Effect of oil phase concentration on beverage emulsions stability
Tabela 1. Wpływ zawartości fazy olejowej na stabilność emulsji napojowych

Oil phase Faza olejowa %	Size index Indeks wielkości cząstek R		Opacity Stopień zmętnienia O		Droplet size Wielkość kuleczek olejowych $D_{[4,3]}$, μm	Storage test Test prze-chowalniczy
	0 weeks 0 tyg.	12 weeks 12 tyg.	0 weeks 0 tyg.	12 weeks 12 tyg.		
Arabic gum – Guma arabska						
20	0.48[e]	0.49[e]	1.06[d]	1.12[d]	0.57	+
30	0.75[g]	0.77[h]	1.63[g]	1.66[f]	4.87	+
40	0.84[h]	0.88[i]	1.77[h]	1.71[f]	4.69	+
Modified starch – Skrobia modyfikowana						
20	0.27[b]	0.30[b]	0.63[b]	0.76[b]	0.71	+
30	0.43[d]	0.44[d]	1.23[e]	1.30[e]	0.76	+
40	0.63[f]	0.63[g]	1.69[gh]	1.69[f]	1.18	+
Ghatti gum – Guma ghatti						
20	0.21[a]	0.23[a]	0.50[a]	0.60[a]	0.45	+
30	0.30[c]	0.33[c]	0.88[c]	0.98[c]	0.42	+
40	0.49[e]	0.59[f]	1.40[f]	1.77[g]	0.52	+

Mean values denoted by different superscripts in the same column differ significantly from each other ($\alpha = 0.05$).
Wartości średnie oznaczone różnymi indeksami w tych samych kolumnach różnią się między sobą statystycznie istotnie ($\alpha = 0,05$).

The increase of oil phase concentration in range from 20 to 40% in case of emulsions stabilized by gum ghatti as well as these with addition of modified starch did not cause any significant changes neither in particle size distribution nor in the average oil droplet size (Fig. 2, Table 1). That is why we can assume that beverage emulsion stability with addition of 40% of disperse phase will be as high as emulsion with 20% addition. Storage test partly proved these assumptions. Emulsions with addition of gum ghatti and
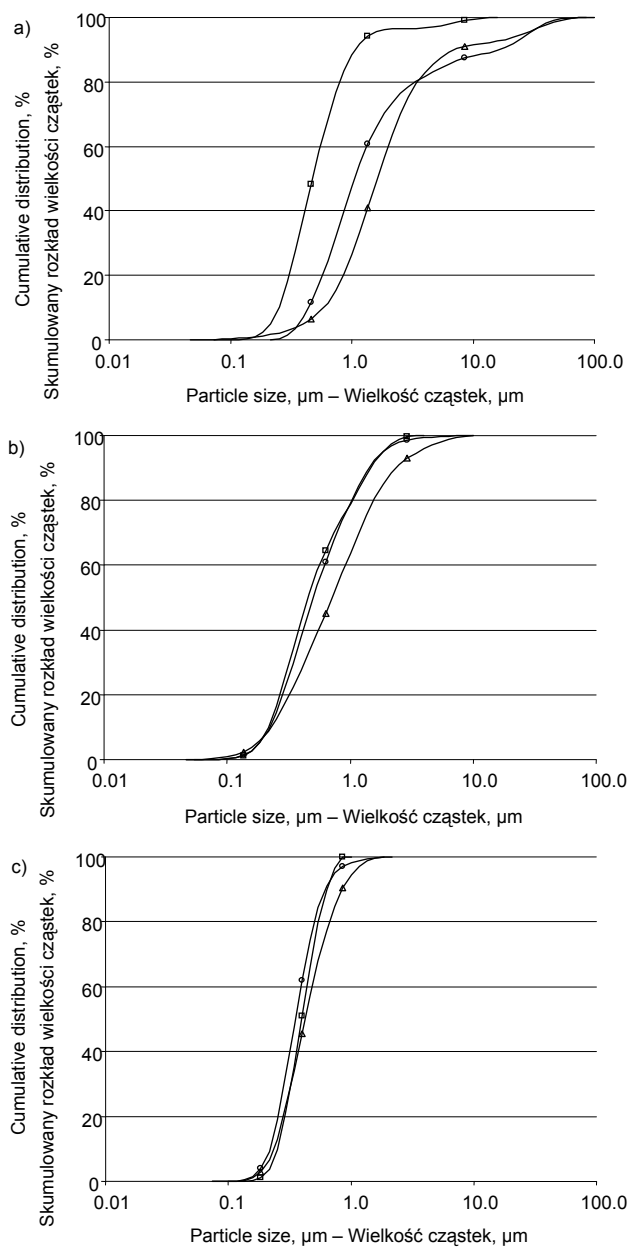
Fig. 2. The size distribution of the dispersed phase particles in beverage emulsions with: a) arabic gum, b) modified starch, c) ghatti gum. Oil concentration, %: □ – 20, ○ – 30, Δ – 40

Rys. 2. Rozkład wielkości cząstek fazy zdyspergowanej: a) emulsje stabilizowane gumą arabską, b) emulsje stabilizowane skrobią modyfikowaną, c) emulsje stabilizowane gumą ghatti. Stężenie fazy olejowej, %: □ – 20, ○ – 30, Δ – 40

the obtained from them beverages were stable for at least three months. On the other hand in case of emulsion with addition of modified starch with 30 and 40% addition of oil phase a little decrease of stability was found. In beverages obtained from emulsions mentioned above after 3 months a small amount of sediment was found (Table 2).

Table 2. Effect of oil phase concentration on beverages stability
Tabela 2. Wpływ zawartości fazy olejowej na stabilność napojów

Oil phase Faza olejowa %	Size index Indeks wielkości cząstek R		Opacity Stopień zmętnienia O		Storage test Test przecho-walniczy
	0 weeks 0 tyg.	12 weeks 12 tyg.	0 weeks 0 tyg.	12 weeks 12 tyg.	
Arabic gum – Guma arabska					
20	0.40[d]	0.36[c]	0.89[c]	0.77[d]	+
30	0.66[g]	0.61[f]	1.44[e]	1.38[f]	+
40	0.82[h]	0.79[g]	1.56[f]	1.51[g]	+
Modified starch – Skrobia modyfikowana					
20	0.31[c]	0.26[b]	0.89[c]	0.42[b]	+
30	0.40[d]	0.34[c]	1.44[e]	0.82[d]	–
40	0.60[f]	0.53[e]	1.56[f]	1.26[e]	–
Ghatti gum – Guma ghatti					
20	0.21[a]	0.19[a]	0.44[a]	0.34[a]	+
30	0.28[b]	0.25[b]	0.83[c]	0.68[c]	+
40	0.54[e]	0.47[d]	1.51[f]	1.32[ef]	+

Mean values denoted by different superscripts in the same column differ significantly from each other ($\alpha = 0.05$).

Wartości średnie oznaczone różnymi indeksami w tych samych kolumnach różnią się między sobą statystycznie istotnie ($\alpha = 0,05$).

Data shown in Table 1 and 2 allow to make a statement that independently of the kind of used emulsifier when the disperse phase concentration was higher the emulsion and beverage opacity was higher. It is an advantageous effect, because when the opacity of beverages is higher the beverages are more similar to natural juices. The obtain results are compatible with the literature. Hernandez and Baker [1991] said that opacity of emulsion depends on oil droplets size as well as on concentration of oil in emulsions, with the increase of oil phase volume fraction the degree of opacity increases. According to the literature [Ray et al. 1983] usually in emulsions and beverages in period of their storage the decrease of opacity is observed, it is interpreted by both the aggregation of oil droplets and the change of refractive index of oil and aqueous phases. In this work a small decrease of opacity of all analysed beverages was noted (Table 2). The decrease of opacity of beverage emulsion in its diluted form could be among others caused by loss of polysaccharides molecules (desorption) from external layers of film formed on the interfacial surface, what caused the change of refractive index of disperse phase. The increase of value of particle size index R with the increase of disperse phase

concentration, observed in all samples of emulsions and beverages independently of the kind of the used emulsifier (Table 1 and 2), cannot be linked only with the decrease of emulsion stability. Only when the level of oil in emulsion is constant the higher value of index R is a result of only the increase of droplet size and can show deterioration of emulsion stability [Reineccius 1994]. However, the increase of index R was at least partially caused by the increase of particle size of disperse phase, which can be confirmed by the results of measurement of a particle size by the laser scattering method.

CONCLUSIONS

1. The increase of oil phase addition in range from 20 to 40%, independently of the kind of used emulsifier, caused the increase of apparent viscosity of beverage emulsion and the beneficial increase of both emulsions and beverages opacity.

2. The influence of oil phase concentration on emulsion stability depended on the kind of the used emulsifier. In case of emulsions with addition of gum ghatti no changes of stability were observed. In case of emulsions with addition of modified starch the low decrease of beverages stability was observed. The highest changes were observed in emulsions with addition of gum arabic.

3. The observed considerable increase of mean oil droplet size with increasing of oil phase concentration as well as the considerable extension of oil droplet size distribution could be the reason of breaking gum arabic emulsions before expiring of the required period of emulsion stability (6 months) in soft drink industry.

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WPŁYW ZAWARTOŚCI FAZY OLEJOWEJ NA CECHY REOLOGICZNE I STABILNOŚĆ EMULSJI NAPOJOWYCH

Streszczenie. Przedmiotem badań było określenie wpływu zawartości fazy olejowej na cechy reologiczne i stabilność emulsji napojowych z dodatkiem wybranych hydrokoloidów. Emulsje stabilizowano gumą arabską, gumą ghatti oraz skrobią modyfikowaną. Stabilność emulsji określano metodą dyfrakcji laserowej oraz metodą turbidymetryczną. Test przechowalniczy emulsji i napojów prowadzono przez 12 tygodni. Mierzono lepkość pozorną emulsji napojowych. Zwiększenie ilości dodatku fazy olejowej w zakresie od 20% do 40%, niezależnie od rodzaju zastosowanego emulgatora, wpłynęło na wzrost lepkości pozornej emulsji napojowych oraz stopnia zmętnienia zarówno emulsji, jak i napojów. W wypadku emulsji z dodatkiem gumy ghatti nie zaobserwowano zmian stabilności, w emulsjach z dodatkiem skrobi modyfikowanej zaobserwowano niewielki spadek stabilności napojów, największe zmiany stwierdzono w emulsjach z dodatkiem gumy arabskiej.

Słowa kluczowe: emulsje napojowe, stabilność, lepkość, guma arabska, guma ghatti, skrobia modyfikowana