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Influence of pH on Properties the Selected Hydrocolloids Stabilized Model Beverage Emulsions

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Abstract: The aim of this study was to determine the effect of pH , arabic gum, ghatti gum and modified starch additives on stability of beverage emulsions. Stability of emulsions was determined on the basis of the characteristics of particle size of dispersed phase vs. emulsion pH and on the basis of results of emulsion time to breakage measurement. Stability of beverage emulsions with arabic gum or mixture of arabic gum and ghatti depended on pH. With the decrease of pH of emulsion in the range of 5.0 to 2.0 the decrease of stability of emulsion was observed. This dependency was not observed for emulsions stabilized by ghatti gum only.

Key words: Beverage emulsions, arabic gum, ghatti gum, modified starch

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INTRODUCTION

Beverage emulsions are oil-water emulsions that are normally prepared as a concentrate and then diluted in sugar solution in order to produce the finished beverage[1,2]. The emulsion in both its concentrated and diluted form must have a high degree of stability. In soft drinks the beverage emulsion may provide flavour, colour and suitable cloudy appearance[3]. A typical composition includes flavour oils and weighing agents in the oil phase and water, hydrocolloid, citric acid, preservatives, colourings and sweetener in the water phase[4,5]. Hydrocolloids serve as emulsifiers and stabilizers in beverage emulsions. They stabilise emulsions through viscosity effects, steric hindrance and electrostatic interactions[5]. Hydrocolloids suitable for this purpose must have high solubility in cold water, low viscosity in solution, high emulsifying capacity and no thickening and/or gelling effects with aging[6]. Gum arabic and hydrophobically modified starch are the most commonly used hydrocolloids in flavour beverage emulsions[1,7,9].

Emulsion instability results from physical processes, i.e. flocculation, coalescence, Oswald ripening and gravitation separation. The rate of these changes can be measured by determining the size and distribution of oil droplets in the emulsion[10,12]. Many oil-in-water emulsions may be stabilized against flocculation by using electrically charged emulsifiers which generate an electrostatic repulsion between the droplets. The state of flocculation of the droplets is dependent on the interactions between stabilising layers, which in turn depends on factors such as the biopolymer surface coverage, the layer thickness, the surface charge density and aqueous solution conditions, especially pH, ionic strength and divalent ion content[7].

The purpose of this study was to determine the pH effect on the stability of beverage emulsions with addition of the selected hydrocolloids.

MATERIALS AND METHODS

Materials: Gum arabic samples (Valgum and Valspray A) and rosin esters samples were provided by the Valmar, France. Ghatti gum was obtained from Hortimex, Poland. Modified starch (Purity Gum 2000) was obtained from the National Starch and Chemical. Essential oil was purchased from JAR, Poland. Sodium benzoate and citric acid food grade from Orffa Food Eastern Europe. Distilled water was used to prepare solutions and emulsions.

Emulsion preparation: Emulsion concentrates were prepared according to the following formula: essential oil - 10% (w/w), weighing agent (rosin esters) 10% (w/w), emulsifier (gums) 5% (w/w) or modified starch 12% (w/w), sodium benzoate 0.1% (w/w), citric acid and distilled water up to 100% (w/w). The emulsifiers were dispersed for half an hour with an RW 20 DZW mixer by Janke and Kunkle, Germany, in water at 20°C

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(modified starch) or 40°C (gums), in which the sodium benzoate had been previously dissolved. The water phase was stored for 24 h to hydrate emulsifier. Pre-emulsion was prepared by adding together the water and oil phase (i.e., the hydrocolloid solution and the essential oil with weighing agent) and stirring with the mixer RW 20 DZM for 15 min with the velocity 1700 rpm. At this point, the pH of the premixes was adjusted to 5 or 4 or 3 or 2 with 2 M citric acid. A fine emulsion was achieved by subjecting the premixes to a two-stage homogenization with an APV-1000 homogenizer by APV, Denmark, at 55 MPa in the first stage and 18 MPa in the second stage.

Mean particle size and particle size distribution: of beverage emulsions were determined in the range 0.12 – 704 ìm by laser scattering using Microtrac Partical Size Analyzer (Leed's and Northrup, USA) the next week after preparation. The emulsions were diluted 1:200 with distilled water.

Electrical potential (ζ): was determined using a Malvern Nano ZS (Malvern Instruments Ltd., Malvern, UK) the next week after preparation. The emulsions were diluted with distilled water. Zeta potential was measured by electrophoresis method. In electrophoretic mobility measurements were used such effects as: laser doppler velocimetry and phase analysis light scattering.

Emulsion stability: In order to determine the emulsion stability end-point (time to breakage) the emulsions were diluted in 5% sugar solution and stored in 1L plastic bottles (PET) at room temperature and daylight. The absorbance was read at 500 nm, using a Helios β spectrophotometer (Unicam, UK). A 5% sugar solution was used as a blank sample for absorbance measurements. Samples were consistently taken from a point at 4 cm from the bottom of the bottle. Daily readings were performed until a week from the first reading. The first-order logarithmic model has been used to the mathematical description of the absorbance vs. time relation.

A first-order model is characterized by the following equation: $\ln A = \ln A_0 - k_1 t$,

where t is time, A absorbance at time=t, A_0 absorbance at time=t_0, k_1 the first-order rate constant. Emulsion stability (time to breakage) was computed from the above fitting equation at $A = 0.1\ A_0$[1].

RESULTS AND DISCUSSION

The limitation of destabilization processes in beverage emulsions can be achieved, among other things, by obtaining the proper dispersion degree. The emulsion stability was greater when the droplet size was smaller. An emulsion containing weighing agents and an acceptable emulsifying constituent will typically not separate if the average particle size of the emulsion is below than 1 µm[4].

Table I. Effect of pH on emulsion stability

	Droplet size (ìm)			Potential ζ	Time to breakage
pH	$D_{[V\ 0.1]}$	$D_{[V\ 0.5]}$	$D_{[V0.9]}$	(mV)	(days)
Arabic gum					
5	0.43	0.65	0.97	- 35.8	318
4	0.50	0.72	1.01	- 29.2	236
3	0.42	0.76	9.01	- 14.9	124
2	0.49	0.79	10.9	- 17.2	200
Ghatti gum					
5	0.23	0.37	0.64	- 26.5	216
4	0.24	0.39	0.71	- 26.5	216
3	0.24	0.40	0.72	- 26.5	216
2	0.24	0.43	0.97	- 28.2	316
Arabic gum +Ghatti gum					
5	0.25	0.37	0.59	- 39.1	185
4	0.30	0.46	0.77	- 29.3	169
3	0.27	0.46	28.7	- 20.1	145
2	0.28	0.42	9.15	- 17.8	139
Modified starch					
5	0.39	0.82	1.70	- 31.1	285
4	0.39	0.83	1.86	- 24.6	213
3	0.43	0.92	1.80	- 34.8	247
2	0.57	1.15	2.19	- 8.5	180

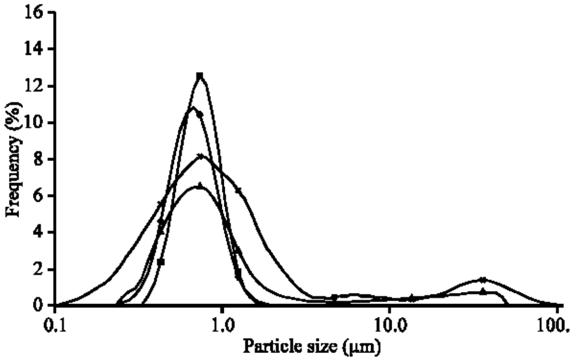

Fig.1: The size distribution of the dispersed phase particles in beverage emulsions with arabic gum -◆-◆- pH=5.0, - ■ -■ - pH=4.0, - ▲-▲- pH=3.0, -x-x- pH=2.0

In Present investigations pH of emulsions was adjusted in the range of 5.0 to 2.0.

The run of curves (Fig. 1) obtained for volume fractions of particles with given size shows that emulsions at pH 5.0 and 4.0 contained oil droplets in the size from 0.3 to 1.8 µm. Any essential differences were observed in the size distribution of particles of the dispersed phase in these emulsions. The decrease of pH to 3.0 and more to 2.0 caused the appearance of larger aggregates of particles in emulsion samples. In emulsion at pH=3.0 the largest oil

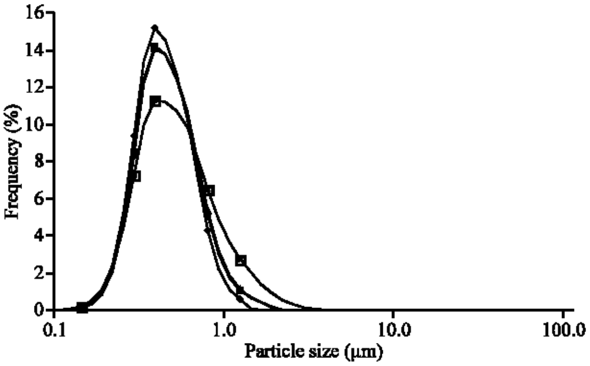

Fig. 2: The size distribution of the dispersed phase particles in beverage emulsions with ghatti gum
-◆-◆- pH=5.0, - ■ -■ - pH=4.0, - ▲-▲- pH=3.0, -x-x- pH=2.0

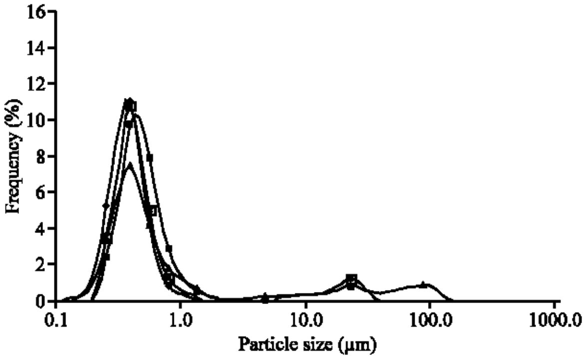

Fig.3: The size distribution of the dispersed phase particles in beverage emulsions with mixture of arabic gum and ghatti gum
-◆-◆- pH=5.0, - ■ -■ - pH=4.0, - ▲-▲- pH=3.0, -x-x- pH=2.0

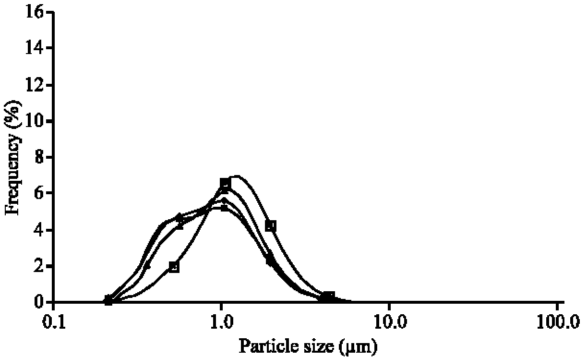

Fig. 4: The size distribution of the dispersed phase particles in beverage emulsions with modified starch
-◆-◆- pH=5.0, - ■ -■ - pH=4.0, - ▲-▲- pH=3.0, -x-x- pH=2.0

droplets were with diameter about 40 μm and in emulsion at pH=2.0 with the size more than 70μm. Approximately 90% of the droplets in the emulsion samples at pH 5.0 and samples at pH 4.0 were under 1 μm in diameter, but in emulsion samples at pH=3.0 and samples at pH=2.0 were under 10 μm (Table I). Considering the pH effect on the size distribution of particles in emulsion, it was pointed out that the decreasing of pH from 5 to 2 intensified the flocculation phenomena resulting in nucleation of larger particles of dispersed phase, which reduced significantly the stability of beverage emulsions. The time to breakage of emulsion at pH=5.0 was 318 days while for emulsion at pH=2.0 only 200 days (Table I). There was significantly less stability for the emulsions at pH=2.0 than for those at higer pH. It appeared that the higher ionic strength at pH=2.0 due to the addition of H^+ for pH adjustment was significant enough to promote instability due to a shielding effect from the counter – ions in the water phase on the charges over the droplet surface, as compared to emulsions at higher pH levels[5]. The similar results were obtained by investigating the influence of pH on the size distribution of oil droplets in the emulsion obtained with addition of mixture of arabic gum and ghatti in rate 1:1. In the samples of emulsion at pH= 5.0 and pH=4.0, over 90% of oil droplets had the diameter below than 1 μm. Thus the condition of emulsion stability suggested by Buffo. A significant spread of particle size distribution of dispersed phase was observed in the sample of emulsion at pH=3.0 (Fig. 3). In this emulsion the aggregates of particles overcame even the size of 100 μm and 10% of particles were larger than 28 μm (Table I). It was the reason of decreasing the emulsion stability. The times to breakage for emulsion at pH=3.0 and pH=2.0 were 145 and 139 days, respectively. Comparison of the stability of arabic gum emulsion with the stability of those made of arabic gum and ghatti showed no improvement of emulsion stability induced by synergetic effect (Table I).

The samples stabilized by arabic gum appeared to be more stable than those stabilized by the mixture of arabic and ghatti gums. The analysis of measurement data for stability of the emulsion with addition of ghatti gum only suggested that the stability of emulsion with mixture of arabic gum and ghatti is higher that those with arabic gum. The size distribution of particles in emulsions stabilized by ghatti gum did not change significantly with decreasing of pH in the range from 5.0 to 2.0 (Fig. 2). But the time to breakage of emulsion at pH 2.0 was even larger than for emulsion at pH 5.0 (Table I).

In the case of beverage emulsion stabilized by modified starch no significant effect of pH on the particle size distribution was observed (Figure 4). In the samples of emulsion at pH=5.0 there were the particles with size

0.22 μm up to 4.24 μm, while in the samples at pH=2.0 we found particles with diameters from 0.26 μm to 5.04 μm. Independently of pH in all emulsions with addition of modified starch approximately 90% oil droplets had a diameter less than 2 μm (Table I). Nevertheless, the time to breakage decreased with decreasing pH of modified starch emulsions (Table I). The hydrocolloids applied stabilise emulsions through viscosity effects, steric hindrance and electrostatic interactions. In the case of modified starch the dominant mechanism of emulsion stability was the steric stabilization, therefore the electrostatic forces seem not to take on the significant role in the emulsion stabilization[8]. For this reason the change in pH of emulsion toward more acid did not induce the increase of velocity of flocculation and in consequence it lead to appearance of aggregates of particles in emulsions at lower pH. This phenomenon was observed in the emulsions stabilized arabic gum or mixture of arabic gum and ghatti.

In the case of arabic gum the electrostatic and steric stabilization occurs simultaneously, but the presence of negative charged groups on the surface of arabic gum molecules indicates that the primary stabilization mechanism is electrostatic in character[13]. Interaction between dispersed oil droplets is dependent on the electrical potential which is called the zeta potential. When a cationic electrolyte is added to an emulsion containing a dispersed phase carrying negative charges, the electrolyte will be absorbed and neutralize the zeta potential. The emulsion with arabic gum should have a zeta potential more negative than 30 mV to be stable[1]. With decreasing of pH of emulsion stabilized by arabic gum or mixture of arabic and ghatti gums the significant change in the zeta potential was observed (the negative zeta potential decreased to zero). But for the emulsions with addition of ghatti gum the zeta potentials did not change with decreasing pH of emulsion (Table I). It is possible that for this reason the stability of emulsion with addition of ghatti gum did not decrease together with decreasing of pH.

CONCLUSIONS

Stability of beverage emulsions with addition of arabic gum or mixture of arabic gum and ghatti depended on pH. The decrease of stability of emulsions was observed with the decrease of pH in the range of 5.0 to 2.0. In the case of emulsions with addition of modified starch influence of pH on stability was considerably lower and in the case of emulsions stabilised with ghatti gum no influence of pH on stability was observed.

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