



STABILITY OF SOME FLAVOR EMULSIONS AGAINST GRAVITATIONAL SEPARATION AFTER REDUCING THE AMOUNT OF GUM ARABIC IN THE FORMULATION

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ABSTRACT

Gum Arabic (GA), a natural plant extract, is frequently used for the preparation and stabilization of flavor emulsions that is commonly used in soft drink and flavored beverage industry. This study aimed to reduce the amount of GA in some flavor model emulsions for cost effectiveness and studying the effect of that on the stability of these emulsions against gravitational separation during storage. Five flavor model emulsions were formulated using pure citral and cinnamic aldehyde and their mixtures at different weight ratios. Results indicated that a flavor/gum ratio 1:1 or 1:0.5 was not able to stabilize the particle size of all emulsions which is manifested by increase in size by many folds during storage. Similarly, four of the flavor model emulsions showed instability behavior (creaming or sedimentation) toward gravitational separation at the same flavor/gum ratios.

However, only one flavor model emulsion out of the five models showed a high stability against gravitational separation at flavor/gum ratio 1:1 or even 1:0.5. That emulsion model was characterized by having a density matching (similarity) between its dispersed flavor phase and its continuous water phase. This indicates the possibility of formulating some flavor emulsions with reduced amounts of gum Arabic only by matching the density between the flavor phase and the continuous phase of the emulsion.

INTRODUCTION

Gum Arabic (GA) is the dried gummy exudation obtained from various species of *Acacia* trees like

Acacia senegal and *Acacia seyal* which belong to the Leguminosae family (Martin, 1969). GA is extensively used to stabilize the concentrated flavor oil emulsions which is used to impart flavor to beverages and soft drink industries (Given, 2009, Mirhosseini *et al* 2008a,b and D'Angelo, 2006). Randall *et al* (1988) indicated that the emulsifying properties of GA originate from the proteinacious fraction content of the gum namely arabiogalatan protein and glycoprotein. The proteinacious fraction represents only 10% of the total gum molecule though; it contains most of the gum protein (Thevenet, 1988). That fraction has surface active properties thus it decreases the interfacial tension between the flavor oil and water which stabilizes the emulsions. The proteinacious fraction is also responsible for imparting charge repulsion between oil droplets in the emulsion which prevents them from flocculation and coalescence leading to more emulsion stability (Jayme *et al* 1999). Beside the proteinacious fraction, GA also contains arabinogalactan fraction which represents 90% of the gum molecule and composed of complex polysaccharides (Thevenet, 1995). This fraction is characterized by low viscosity and high solubility in water and most of all it has an excellent film forming properties around the oil droplets. This prevents droplets from coalescing, thus it contributes further to the emulsions stability. Another advantage of using GA to stabilize flavor emulsions is that it is more stable toward droplet flocculation in the presence of electrolytes (Mc Clements, 2004), which is not the case with protein-stabilized flavor emulsions. However GA is considered to be a poor emulsifier compared with other pure proteins derived from milk (e.g whey protein, casine, sodium caseinate). Thus the amount of GA should be increased to about ten times to get the same emulsion stability as that of the corresponding protein-

stabilized emulsion (Dickinson and Galazka, 1991). For this reason the oil:GA ratio of 1:2.0 (Williams and Phillips, 2000) or 1:2.5 (Thevenet, 1995) or even 1:3 (McClements, 2005) is usually used to stabilize flavor oil emulsions.

Due to the fluctuation of the GA supply and prices, a strong trend is growing in the industry to replace it with another steady supply and affordable emulsifiers (Seisun, 2002). Starch derivatives were found to be a potential candidate for substituting GA (Taherian *et al* 2006 and Tesch *et al* 2002). This group of synthetic surface active starches showed good emulsifying properties but the natural identity provided with GA can not be fulfilled with these synthetic starches. Recently, other natural substitutes of GA were investigated like corn fiber gum (Yadav *et al* 2009, 2007) and covalently bonded milk protein–maltodextrin conjugates (Akhtar and Dickinson, 2007).

Beside gum substitution, a trend is developed to reduce the amount of GA in the beverage emulsions. This can also help in slowing down the depletion of the affordable market supply but that will be on the expense of emulsion stability. It was found that the minimum amount of GA that can stabilize O/W emulsion is 1:1 wt% (based on soy bean oil, McNamee *et al* 1998). Further reduction of the amount of GA leads to dramatic increase in the particle size and emulsion separation.

On the same trend of reducing the amount of GA in flavor emulsions, the author aimed in this investigation at studying the stability behavior of some flavoring model emulsions against gravitational separation, using low amounts of GA. The flavor model is composed of citral, cinnamic aldehyde and their blends at different weight ratios. The flavor to gum weight ratio used was 1:1 and 1:0.5. All the formulations were prepared using GA as a sole emulsifier.

MATERIALS AND METHODS

Chemicals

Gum Arabic from Acacia tree (reagent grade. CAS No. 9000-015), *trans*-Cinnamic aldehyde (99.0+%, CAS No.14371-10-9) and citral (95.0% CAS No. 5392-40-5) were purchased from Sigma-Aldrich Inc. (St. Louis, MO, USA).

1- Preparation of the flavoring model blends

The flavoring models (as an oil phase in the emulsion) comprised five different blends which

were composed of pure citral and cinnamic aldehyde either alone or in combination with each other at different weight ratios as given in Table (1). The five flavoring blends were denoted in this investigation by B1, B2, B3, B4 and B5.

2- Preparation of the flavoring emulsions

Two main groups of emulsions of different flavoring material : GA ratios were prepared. The first group: was formulated using a weight ratio of flavor: GA = 1: 1. The second group of emulsions was formulated using weight ratio of flavor : GA = 1: 0.5.

The two groups of emulsions were formulated using the same amount of the flavoring model blends as oil phases. Details of the emulsion groups and the emulsion formulae were tabulated in Table (1).

The emulsion was prepared by allowing GA to hydrate in distilled water with gentle stirring using magnetic bar followed by the addition of the flavoring blend. The emulsions were pre-homogenized for 2 minutes at 20,000 rpm using high speed homogenizer (tissue terror model 985370-395, Biospec products, Inc). Then they were microfluidized for 5 cycles using microfluidizer (M-110Y microfluidic, Newton, MA). The inlet air pressure was 75 psi (~ 510 kPa) at the regulator gauge which was magnified (x 232) inside the interaction chamber to reach 17400 psi (~119.9 MPa). The emulsions were cooled during the microfluidization cycles using an ice bath. Finally, the emulsions were stored in dark glass bottles. Certain volumes of each emulsion were carefully transferred into flat-bottom cylindrical glass tubes (100 mm height) designed especially to fit into optical scanning instrument (Turbiscan) to investigate emulsion stability through backscattering measurements as will be discussed later. All preparations were stored for 1 week at 4°C.

3- Measurement of emulsion stability

Emulsion stability against gravitational separation (creaming or sedimentation), was measured by using the instrument for the optical characterization of a liquid dispersion (Turbiscan classic MA 2000, formulaction, Toluse, France). The fresh emulsions were contained in a cylindrical glass measurement cell with flat-bottom which is completely scanned from bottom to top with a light source (near infrared $\lambda=850\text{nm}$). Two synchronous detectors collect transmission and backscattering

data and reading head scans the entire length of the sample (about 55 mm) acquiring transmission and backscattering every 40 μm . A transmission detector receives the light that goes through the sample while the backscattering detector receives the light backscattered by the sample. A pattern of the light flux as a function of the sample height is obtained. The results are reported as creaming/sedimentation backscattering value profile versus emulsion height. An increased backscattered light at the bottom of the cell means sedimentation while a decrease backscattered light at the bottom means creaming

Scans were performed for all emulsions at the zero time, just after preparation, and then after 1 week of storage at 4°C. Each scans provided a curve and all curves are overlaid on one graph to show stability at the end of storage period.

4- Measurement of particle size

Particle size was measured by using dynamic light scattering Nano-ZS (Nanoseries, Malvern Instruments, UK). Measurements were done at 25°C, with a fixed angle of 172°. Sizes quoted are the z-average mean (dz) for the droplet hydrodynamic diameter (nm). Each sample was measured at least 3 times; data reported was mean \pm S.D

5- Measurements of density

The density of pure citral and pure cinnamic aldehyde and their blends at 25.0: 75.0 weight ratio (blend number B4, **Table 1**) were measured at 27°C \pm 2 using a pyrex Becknometer equipped with a thermometer. First the clean instrument was weight empty then filled with excess distilled water until it came out from the side arm of the Becknometer to evacuate the instrument totally from air bubbles. The instrument was dried using soft tissue from the outside to remove the dripped water traces then re-weight and the difference in weight represents the actual volume capacity of the Becknometer under the conditions of the experiment, considering the density of distilled water is 1. After that, water was evacuated and the Becknometer was washed with absolute alcohol, air dried, weighed empty again, then filled with the target pure citral or cinnamic aldehyde or their blend (B4) and re-weighed. From the weight of the sample and the volume of the Becknometer, the density of the samples was determined. Each experiment was repeated twice.

RESULTS AND DISCUSSION

1- Emulsion stability regarding the particle size

Figure (1) showed the particle size distribution of emulsions containing five flavoring blends stabilized with two different amount of GA at the zero time of storage. Evidently, the emulsion containing 100% GA (flavor/gum ratio 1:1) shows smaller particle size compared with the particle size exhibited by the emulsion containing 50% GA (flavor/gum ratio 1: 0.5). This is not surprising to the author since high GA content reduced the interfacial tension between the water phase and the flavoring oil phase which facilitate breaking down of the flavoring particles into smaller ones during microfluidization. It is worth mentioning that, a high standard deviation among the replicate measurement of particle sizes ranging from ± 7 to ± 40 was observed in all emulsions (data not shown). This may be ascribed to the insufficiency of GA to cover the particles with interfacial monolayer. Thus during microfluidization, some particles which are not fully covered with the gum can re-coalesce (join together) in the interaction chamber of the microfluidizer leading to some larger particles that cause that high standard deviation during particle size measurements. Storing the emulsions samples for one week resulted in dramatic increase in the particle size for all the flavoring emulsion (**Fig. 2**). The increase was pronounced especially for the low gum-containing emulsions (50.0%) compared with the zero time measurements (**Fig. 1**). This indicates that GA even at 100.0% (flavoring/gum 1:1) is not sufficient to keep the small particle size of the emulsions at their initial values before storage (zero time). From these results it is clear that GA amount should be increased more than 100 wt.% (on flavoring basis) in order to cover the surface of all flavoring droplets and hence stabilizes the particle size of the flavor emulsions during storage.

2- Emulsion stability regarding gravitational separation

Fig. (3a) represents the back scattering (BS) patterns of the emulsions containing five flavor model blends that formulated with flavor/gum ratio 1: 0.5 (50.0% on flavor basis), at the zero time of storage. It is shown that the back scattering values were constant across the entire height of the emulsions tubes for all samples, which indicate an initial stability against gravitational separation. However, the BS % value for emulsion containing 100%

Table 1. Composition and formulation of the emulsions and the flavoring model blends

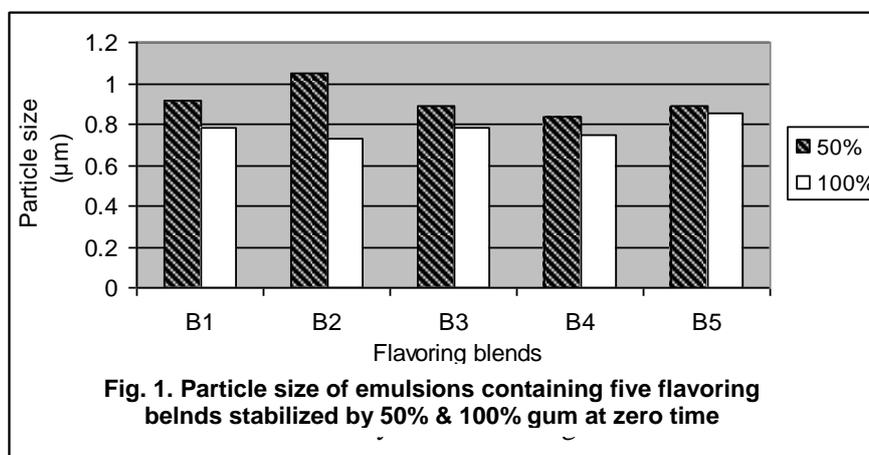
Emulsion groups	
Group I: flavor/gum ratio (1:1)	Group II: flavor/gum ratio (1:0.5)
Formula: water (96g) flavoring blend (2g) gum (2g)	Formula water (97g) flavoring blend (2g) gum (1g)
Flavoring blend	Composition of the flavoring model blends (wt%)
B1	citral 100.0 : cinnamic aldehyde 0.0
B2	citral 75.0 : cinnamic aldehyde 25.0
B3	citral 50.0 : cinnamic aldehyde 50.0
B4	citral 25.0 : cinnamic aldehyde 75.0*
B5	citral 0.0 : cinnamic aldehyde 100.0

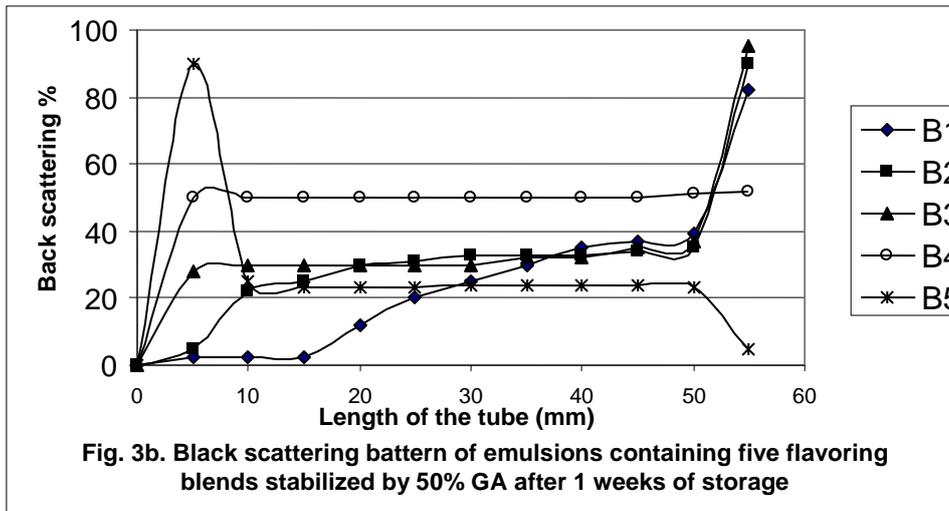
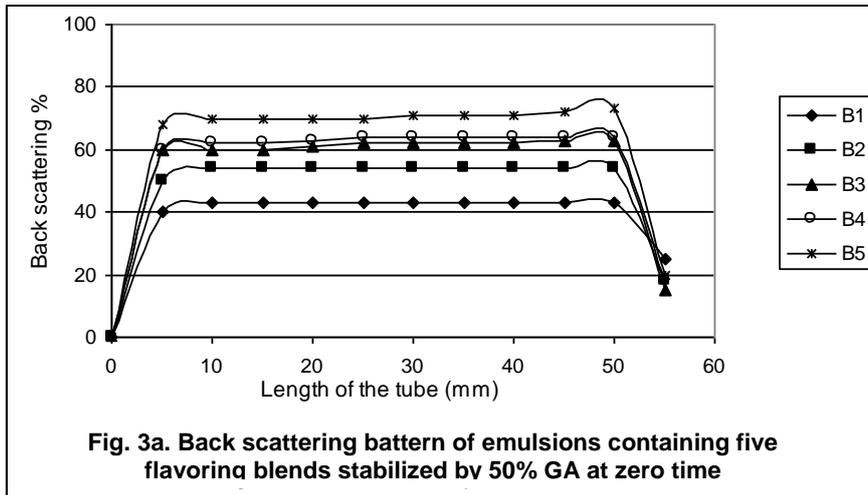
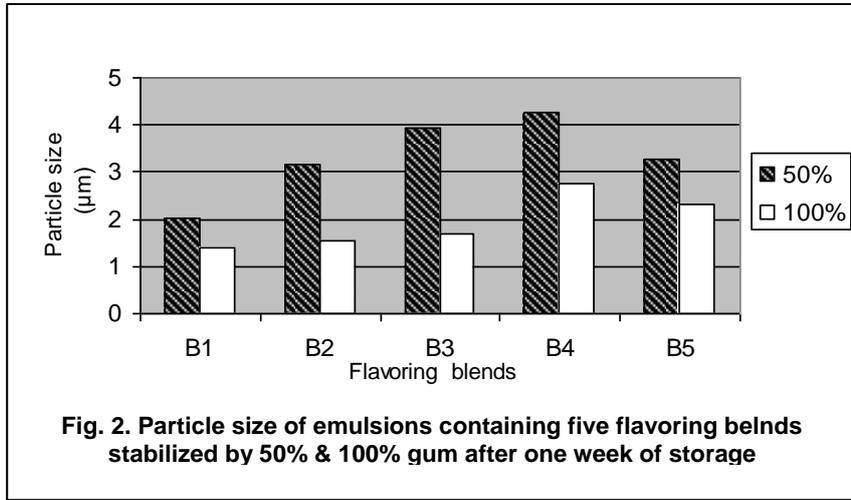
* This wt% ratio is equivalent to molar ratio of 1: 3.531 for citral and cinnamic aldehyde, respectively

Table 2. Density measurements of pure citral, cinnamic aldehyde and their blend (B4)

Density at 27°C				
Flavoring blend (B1) (citral 100.0%)		Flavoring blend (B5) (cinnamic aldehyde 100.0%)		Flavoring blend (B4) (25.0% citral: 75.0% cinnamic aldehyde)
indicated by the manufacturer	experimental	indicated by the manufacturer	experimental	experimental
0.888	0.884	1.05	1.043±0.001	0.998±0.001*

* Very close to the density of distilled water which is 1.000





citral (B1) is less than those of the emulsion containing 100% cinnamic aldehyde (B5). The same trend was found in **Fig. 4(a)** in which the weight ratio of oil/gum is 1: 1 (100.0% on oil basis). This may be attributed to the difference in their refractive indices, i.e. for citral = 1.4876 whereas for cinnamic aldehyde = 1.6209. As the weight fraction of cinnamic aldehyde was increased in the flavoring blends from B1 to B5, the back scattering values also were increased until it reached its maximum at blend B5 (100% cinnamic aldehyde). **Fig. (3b)** showed the stability of the different flavoring emulsions against gravitational separation after storage period of one week. **Fig. (3b)** depicts also that the emulsion containing the flavor model blend B5 (100.0% cinnamic aldehyde) gave the highest BS value (~90.0%) at 5 mm from the bottom of the emulsion tube (left upper side on the graph), indicating high particle density at the bottom. Meanwhile, the same blend (B5) gave the lowest value of BS at 55mm above the bottom of the emulsion tube (~5%, right lower side on the graph), indicating low particle density at the top of the emulsion tube. This is a typical gravitational instability symptom indicating sedimentation of the emulsion due to the high density of its flavoring blend compared with water (B5: cinnamic aldehyde, $d=1.043$, **(Table 2 and Fig. 5)**).

On the contrary, emulsions containing the flavoring blends B1, B2, B3 showed an opposite behavior where the higher particle density was found at the top of the emulsion tube (82%-98%, right upper part on the graph), while the lower particle density was found at the bottom (left lower part on the graph). This pattern is typical gravitational instability symptom indicating creaming of these emulsions due to the low density of their flavoring blends (**Fig. 5**). The same behavior was exhibited for B1, B2, B3 and B-5 (**Fig. 4b**) where the weight ratio of flavoring to gum was 1: 1 (100.0% on flavor basis).

Figs. (3b & 4b) depicts that the emulsion containing the flavor model blend B4 (citral 25.0%: cinnamic aldehyde 75.0%. **Table (1)** showed completely different back scattering behavior compared with those of the other four flavoring blends. The back scattering value was almost fairly constant across the entire height of the emulsion tube compared with the emulsions containing blends B1-B3 and B5. This indicates stability against gravitational separation regardless of the flavor: gum ratio (1:0.5 or 1:1) and regardless of the particle size which was unstable for this flavor blend as shown during the storage period (**Fig. 2**). The plausible

justification of that stability against gravitational separation is based on the probability of density matching (similarity) between the dispersed flavoring components of blend B4 with water which is the continuous phase of the emulsion. This matching can prevent the flavor droplets from creaming or sedimentation leading to stability against gravitational separation. This assumption may be confirmed from the results of density measurement which is shown in **Table (2)**. The density of the flavoring blend is 0.998 g/cm^3 , i.e. almost of the same order of distilled water density (1.0 g/cm^3).

The question now is how the density of blend B4 has reached that value (0.998) although the density of its individual components citral and cinnamic aldehyde is 0.884 g/cm^3 and 1.043 g/cm^3 respectively in their pure states (**Table 2**)? One may assume that blending citral and cinnamic aldehyde in B4 at weight ratios 25.0%: 75.0% (equivalent to molar ratio 1 : 3.531 respectively) was able to change the density of each component in a way that the blend density became 0.998 g/cm^3 . In another words, one component in a certain weight fraction or molar ratio can act as an inherent density adjusting agent (also called: weighting agent) for the other component when both of them blended together. This inherent density adjustment was not fulfilled at the other flavoring blends B1, B2, B3 and B5 may be due to the difference in their weight ratios compared with B4. This justified their instability towards gravitational separation either due to creaming, B1-B3 or sedimentation B5. It worth mentioning that blending citral and cinnamic aldehyde at 0.25: 0.75 wt ratios (B4) may be associated with a change in the molar volume of each component with the resultant blend density being 0.998 g/cm^3 .

Stokes' law governs the relation between the velocity of emulsion separation due to gravity and the density difference between the dispersed oil phase and the continuous water phase as follows:

$$V = \frac{2gr^2(d_1-d_2)}{9\eta_2}$$

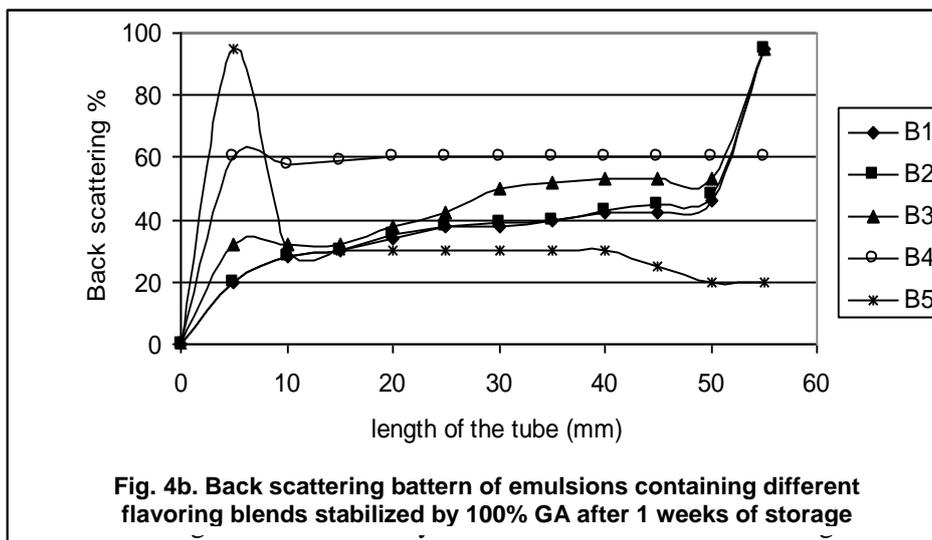
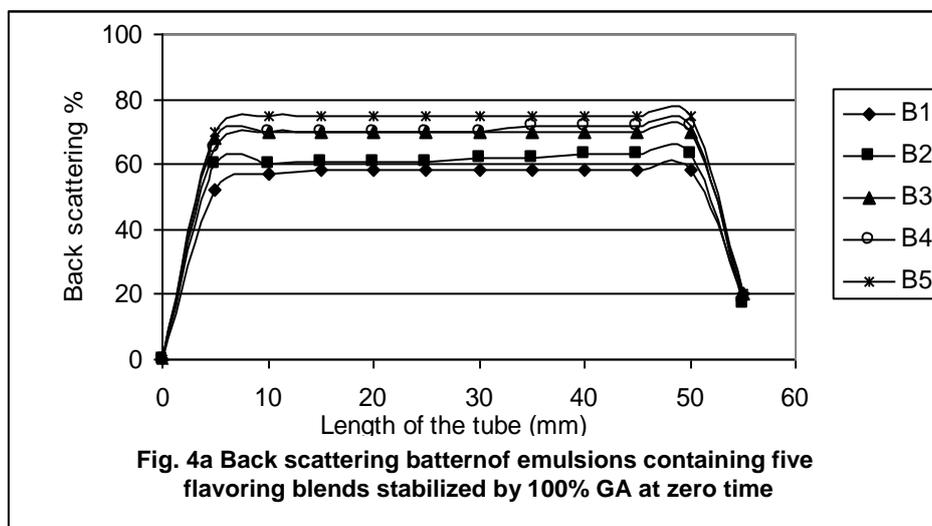
V: velocity or oil droplet movement (creaming or sedimentation)

g: acceleration due to gravity

d_1, d_2 : density of oil and water phases, respectively

r: radius of oil droplet

η_2 : viscosity of water phase



Thus to slow the process of gravitational separation of an emulsion, the numerator in the equation has to be reduced either by reducing the particle size (r) and/or reducing the density difference between the oil phase and water (d_1-d_2) which is the role of weighting agents. Justification of the stability of emulsion containing flavoring blend (B4) against separation may be ascribed to the fulfillment of the above-mentioned conditions.

In soft drink industry, synthetic density adjusting agents (weighting agents) are used to stabilize the flavoring beverage emulsions against gravitational separation (Taherian *et al* 2008 and Chanamai and McClements, 2000). Even when gum Arabic

is used at oil/gum ratio 1:2, density adjusting agents are still needed at 50 wt% (based on oil) to give a stable emulsion (Williams and Phillips, 2000). Examples of these synthetic density adjusting agents are brominated vegetable oil (BVO, $d=1.33$), estergum ($d=1.1$), sucrose acetate isobutyrate (SAIB, $d=1.15$) (Chanamai and McClements 2000). However, some of these agents (e.g. SAIB) are not permitted in certain countries like USA, and others are limited to only 15 ppm in the final product (e.g. BVO). Thus there are some limitations and restrictions of using these density adjusting agents in beverage emulsions.

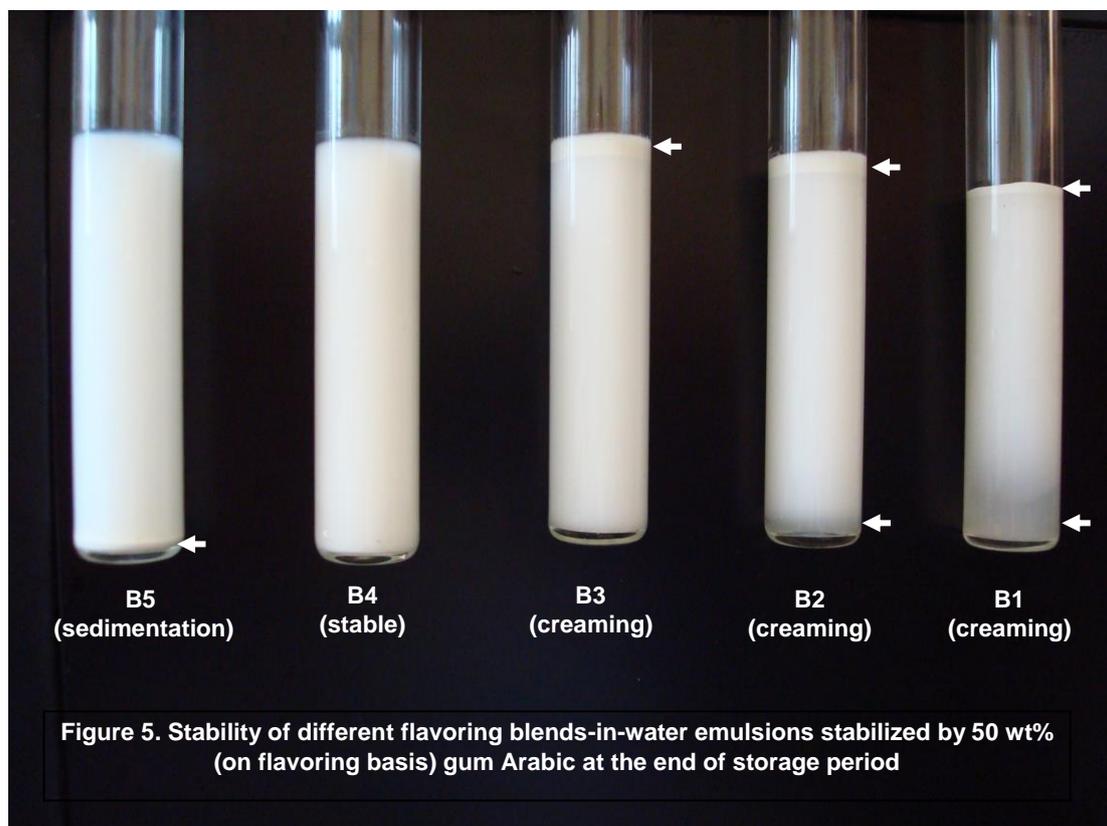


Figure 5. Stability of different flavoring blends-in-water emulsions stabilized by 50 wt% (on flavoring basis) gum Arabic at the end of storage period

CONCLUSION

Reducing the amount of gum Arabic in flavoring model emulsion to 100% or 50% (based on flavor weight) failed to keep the particle size of the dispersed flavor droplets small and stable. These particles grow within one week of storage at 4°C. However, the study also showed that the density of certain flavoring blend can be self-adjusted to match the density of the continuous phase of the emulsion (water), leading to stability against gravitational separation. This can be attained by careful selection of the type of flavoring components, their density and their weight ratios in the blend. If these conditions are taken into consideration, the emulsion can be stable against gravitational separation even at the lowest amount of gum (50.0% on flavor weight). These results have a promising application in formulating flavor emulsions for the soft drink and beverage industry with low gum Arabic content and without need to use synthetic density adjusting agents. This proposal represent a challenge for the flavor technologist to formulate a self-density adjusted flavoring blend that match the

density of the continuous phase in emulsion and at the same time is capable of delivering the desired aroma and flavor impact. That investigation can be further extended in the future to check the stability of these flavor emulsions during longer periods of storage time.

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