Physicochemical and Emulsifying Properties of Barijeh (Ferula gumosa) Gum

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ABSTRACT: *Ferula gumosa Boiss is one of the natural plants of Iran whose exudates (Barijeh) can be used in food industry. In the present study the properties of the gum extracted from tubers of Ferula gumosa were examined. For this purpose, gum was extracted from crude exudates by alcoholic extraction with 90% (v/v) ethanol. The purity of gum was relatively high, and it was composed mostly of polysaccharide. Soybean oil emulsions (10% w/w) were prepared using gum with concentration from 0.2 to 1.0 % (w/w). Surface tension, interfacial tension and creaming measurements were performed for all emulsions. Particle size measurements, light microscopy observations and rheological studies were performed for 1.0 % gum emulsion. The purified gum was found to reduce surface tension and interfacial tension of emulsions. Although particle size distribution measurements showed a slight change in particle size pattern after two month, mean diameter of particles remained constant. The creaming tests confirmed a comparatively good overall stability over a period of two months. The rheological measurements showed the shear thinning nature of emulsions prepared with the Barijeh gum. The emulsion stability was attributed to the surface adsorption mechanism.*

KEY WORDS: *Ferula gumosa, Barijeh gum, Emulsifying activity, Particle size, Ccreaming.*

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INTRODUCTION

Ferula gumosa Boiss is a monocarp plant from the northern sections of Iran. The *Ferula gumosa* is a green annual herb of family Umbelliferrae (Apiaceae) [1]. Among the *Ferula* species present in the area, *Ferula gumosa* has been used more than others and it has more ability to produce oleogum resin of higher quality in comparison with similar species, and it is a good source of pharmaceutical and industrial components. *Ferula gumosa* has a thick sturdy stem that grows up to 3 m height. The stem is glabrous, but gray leaves are hairy [2].

It is a resistant plant, native in humid mountain and semiarid regions of Iran. Its distribution could be observed mostly at an altitude of 2000-4000 m above sea level. It grows in sandy loam. The good quality habitats could be found mostly in north-facing slopes and on calcareous and well-dried soils. The best utilization time is July and August [3, 4].

Barijeh is the air-dried oleo-gum-resin exudation obtained by incising the stems close to the ground. There are two types of gum exudates, the so-called soft and hard ones. The former is generally met with in lumps, consisting of large, irregular masses of brownish color composed of agglutinated tears having a waxy density, but becomes soft and sticky at a temperature between 35 and 37.7 °C. It has a pleasant odor, an acrid taste and freely soluble in diluted alcohol which is its best solvent. Its specific gravity is 1/212 and major components are resinous substances, mucilage and volatile oils. The gum exudates were used in medicine by both oral and topical forms. The drug acts as stimulant, expectorant and vulnerary. In ancient Iranian medicine, the oleogum resin obtained from this plant had been used for digestive disorders and flatulence and topically as a wound-healing remedy [5].

Nowadays, it is used as a food additive than as a drug. It is used as a flavoring additive in food stuffs such as non alcoholic beverages and meat products.

Polysaccharide extracted from Barijeh by alcoholic solution is of interest for some scientists. They identified gum composition by chemical methods. Their analysis showed the presence of galactose, arabinose, rhamnose and uronic acids that galactoronic acid was major component. In addition, their study showed the presence of protein, Calcium and Magnesium.

Barijeh gum forms a low-viscosity solution as well as Arabic gum [6]. *Howlett* (1980) provides a clouding agent base comprising lanolin and a gum resin such as Barijeh gum for cloudy beverages [7]. However, the aim of this investigation was to isolate and characterize the emulsifying properties of gum extracted from *Ferula gumosa* Boiss.

MATERIALS AND METHODS

Plant Materials

The oleogum resin exudates of *Ferula gumosa* were collected from Kopehdagh area in northern Khorasan by cutting up roots from June to July 2005 and kept in refrigerating room. All reagents were of analytical grade. Sulfuric acid (98%), ethanol (95%), glucose and galactoronic acid (HPLC grade) were purchased from Merck, Germany. Soybean oil was prepared from Sigma, USA. Deionized water was used to prepare of solutions and emulsions.

Gum Extraction and Purification

In order to extract the gum from oleo-gum-resin, crude sap was stirred with ethanol 90% for 2 hs. The ethanolic slurry was filtered through Whatman No. 1 filter paper. The residue was washed with ethanol 90% (v/v) twice and then it was dried at 40 °C for 12 hs in vacuum. After drying, the extracted powder was solubilized in distilled water at 50 °C for 2hs and filtered through Whatman No. 1 filter paper. The filtrate was concentrated at 40 °C in vacuum and dialyzed at cut-off 3500 Da. After filtering, solution was concentrated and dialyzed again in the same manner. Finally, the extracted gum was lyophilized (Lyoflex 04, Edwards USA) in -40 °C for the freezing step for 5hs. Then, vacuum (10^{-6} Torr) was applied and when the vacuum was ready, the temperature was switched at 15 degree. After 48 hours the sample was ready.

Fig. 1 shows analytically the stages of the isolation and purification of Barijeh gum.

Gum Characterization

Moisture, crude protein and total ash were measured by A.O.A.C. methods [8]. Briefly, moisture was measured in the form of weight decrease after heating the sample at 105 ^oC for 4 hs. Crude protein was measured by the method of Kjeldal using 6.25 as the conversion rate of nitrogen to crude protein [9]. Total ash was

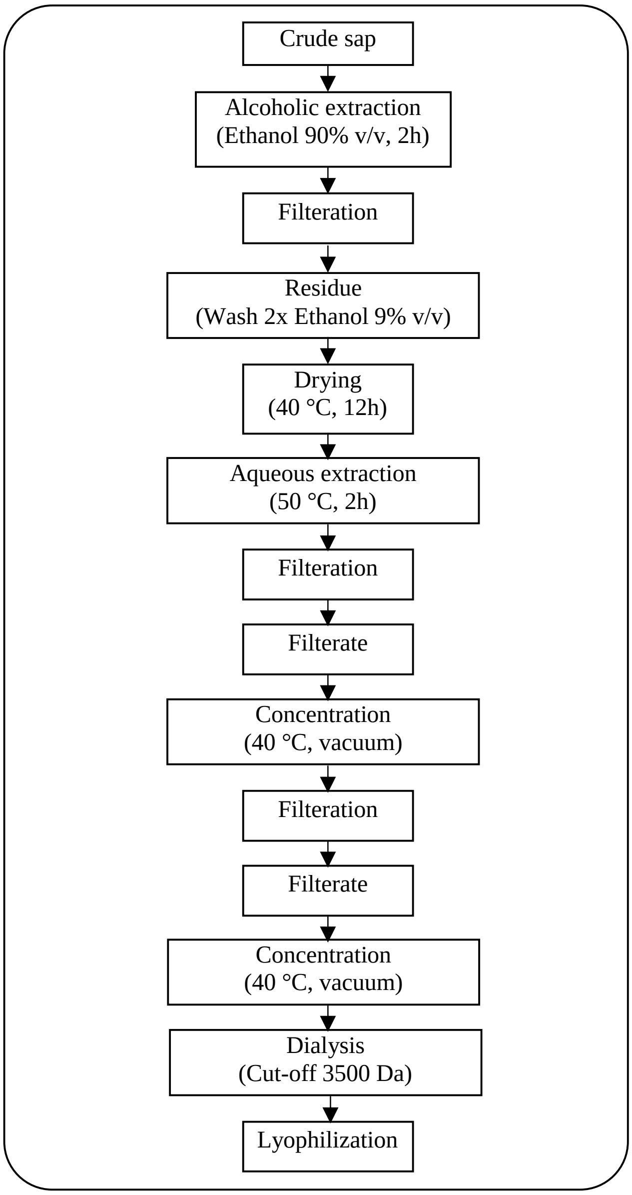


Fig. 1: Extraction–purification scheme of Barijeh oleogum resin.

measured as the residue remaining after heating at 600 ^{o}C for 4 hs. Total sugars and uronic acids were measured by the phenol-sulfuric [10] and *Blumenkrantz* and *Hansen* method (1973) respectively using glucose (Merck, Darmstadt, Germany) and galactoronic acid (Merck, Darmstadt, Germany) as a standard [11].

Emulsion Formation

Ten percent w/w oil-in-water emulsions were prepared with soy bean oil, distilled water and 0.2-1.0 % wt Barijeh gum. Prior to any emulsification process, the aqueous solution of gum was preheated to 50 °C for 10 mins to maximize solubility and solution was cooled to 25 °C. The oil phase was added drop wise to the hydrocolloid solution and emulsification was achieved by shearing for 15 mins using an Ultraturrax T-25 homogenizer (Janke and Kunkel, Germany).

Surface and Interfacial Tension

The surface and interfacial tensions of the gum solutions at different concentrations were measured by the Dü Noüy ring method using a Kruss tensiometer, model K9 (Krüss, Hamburg, Germany) at 25 °C. Before measuring, samples were equilibrated for up to 12 hs. The force acting on the ring was measured as it was moved upward for an air-gum dispersion interface, and as it was moved downward for an oil-gum dispersion interface. The results were plotted against gum concentrations.

Particle Size Distribution Measurement

Size distributions of oil droplets were determined by the laser light-scattering method using a qualsielastic light scattering detector (SEMAtech, Nice, France). This instrument uses the principle of fraunhofer diffraction where a parallel monochromatic beam of laser illuminates the emulsion. The light diffracted by the emulsion droplets gives a stationary diffraction pattern regardless of the particle movement. The particle size distribution of 1% Barijeh emulsions were measured on the first day and two months after preparation at 25 °C.

Light microscopy

The samples for light microscopy were examined and photographed immediately after preparing the 1% Barijeh emulsions under bright field illumination with 40× objective lens on a Zeiss Photo-Microscope 3 (Carl Zeiss,Germany). For the study of time effect, measurements were repeated after 2 months.

Stability Test

Measured amounts of emulsions were poured into graduated cylinders of identical size and stored in a refrigerator. The height of the clear liquid at the bottom of cylinder resulting from creaming was measured at the end also after 24 hs and two months after preparation at 25 °C. The results were plotted against gum concentrations.

Measurement of Apparent Viscosity

The apparent viscosity of emulsions is an important property that determines its use and may be related to its stability. The viscosity of the ten percent w/w oil-in-water emulsions with and without 1% Barijeh as a function of shear rate was determined using a Brookfield viscometer (RVT Model, Brookfield, MA). The measurements were carried out at 25 °C. Values were read on the first day and after two months following the preparation.

Statistical Analysis

All results represent the means of three replicates. Analysis of variance and Duncan multiple range test with $p < 0.05$ were performed using the SAS software.

RESULTS AND DISCUSSION

Gum Characterization

Gum composition is presented in table 1. As shown in table 1, there is a slight difference in Barijeh gum composition when compared to those in the literature. Our results showed 4.3% protein content when compared to that of Jessenne et al. who observed 3.7% protein content [6]. The total sugar content was 83.98%. Therefore, the purity of the gum was relatively high, composed mostly of saccharides. Also gum consisted of uronic acids (galactoronic acid) with a weight ratio of 24.38%. The content of uronic acids obtained in this work was in agreement with that (22.7%) obtained by others [6].

Surface and Interfacial Tension

Surface tension of the continuous phase and interfacial tension, as a function of gum concentration, are shown in Figs. 2 and 3. Surface tension of water at 25 °C was 71.1 mN/m. Addition of 0.2% Barijeh gum decreased surface tension to 65.7 mN/m. Barijeh gum decreased surface tension. Although the effect of increasing gum concentration on decreasing surface tension was significant, this reduction was limited. The two 0.2 % and 0.4 % gum concentrations had significantly less surface tensions than 0.0 % gum concentration and more than the last ones. This result was similar to most gums such as Arabic gum, guar and fenugreek [12-16]. As it was mentioned by several researchers most of the polysaccharides behave as non surface active agents. However, there are some

Table 1: Composition of Barijeh gum.

Barijeh gum	%, w/w
Yield	5.9
Moisture	5.1
Ash	6.0
Protein	4.3
Total Sugar	83.9
From which; Uronic acid	24.3

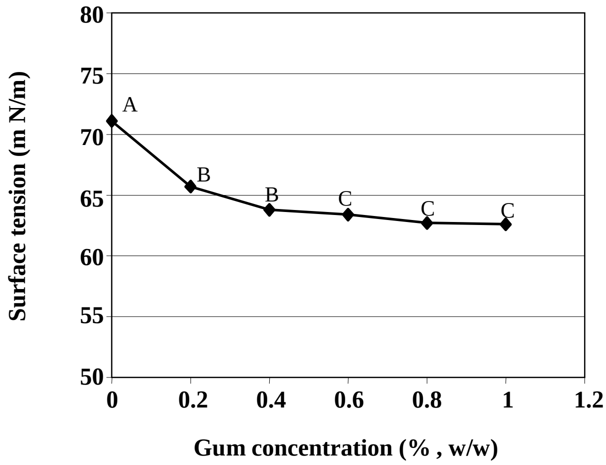


Fig. 2: Surface tensions of Barijeh gum dispersions of various concentrations at 25 °C for 10% soybean.

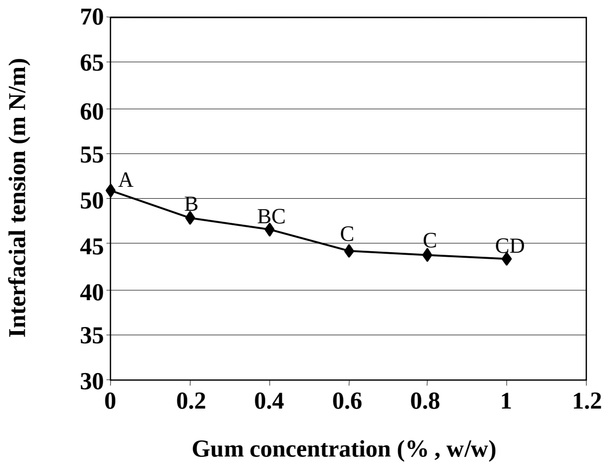


Fig. 3: Interfacial tensions of Barijeh gum emulsions of different concentrations at 25 °C for 10% soybean.

polysaccharides having significant surface activity. Among them, methylcellulose (MC) and hydroxypropyl methylcellulose (HPMC) have already been studied [17].

It was shown that interfacial tensions of 10% soybean oil emulsions in the presence of various concentrations of gum were reduced slightly. The effect of increasing gum concentration on decreasing interfacial tension was significant but this reduction was more limited than the surface tension. As shown in Fig. 3, 0.2 % and 0.4 % gum concentrations had significantly less interfacial tensions than 0.0 gum concentration but more than the other concentrations. Interfacial tension of 10% soybean oil emulsions was 50.8 mN/m at 25 °C Addition of 0.2% Barijeh gum decreased interfacial tension to 47.9 mN/m. Barijeh gum decreased interfacial tension, but this reduction was very limited. Above 0.2 %, interfacial tension reduction of dispersions was rather limited. The interfacial behavior of Barijeh gum was analogous to the behavior observed for surface tension; which clearifies the CMC or critical micelle concentration of gum as a surface active agent or so called surfactant, that is about 0.8% (w/w).

Particle Size Distribution Measurement

Fig. 4 shows the particle size distribution for 1% Barijeh emulsions on the first day and two months after the storage at 25 °C. Particle size distribution was slightly affected after storage time. After two months storage, the particle size distribution curve shifted to the right but the mean diameter of particles remained constant.

Fig. 5 shows the particle size distribution of 1% Barijeh emulsions expressed as cumulative function. Resulting plots appear as S-shaped curves with the emulsion droplets ranging from 0.17-3.42 µm changing to 0.23 -5.14 µm after two months of storage. Our results are in accordance with those obtained for oil-in-water emulsions containing 1% Arabic gum [16]. The particle size where the cumulative distribution is 50% is known as the median droplet diameter ($d_{v,0.5}$). The Barijeh gum had a very small median droplet diameter with 50% of the particles less than 1.18 µm. Table 2 contains the tabulated results for the particle size measurements.

The behavior of the hydrocolloids in emulsion formation and stability is reflected in the size of the formed oil droplets after emulsification. The relative large droplet sizes were attributed to the inefficient gum

Table 2: Mean particle size of 1% barijeh emulsions on the 1st day and after two months storage at 25 °C.

	The 1st day	After two months
Mean diameter [µm]	1.18	1.18
Range [µm]	0.17-3.42	0.23-5.14
Diameter range 0-2.00 µm[%]	90.0	74.5
Particle size distribution	Bell shaped around the mean	Skewed to right

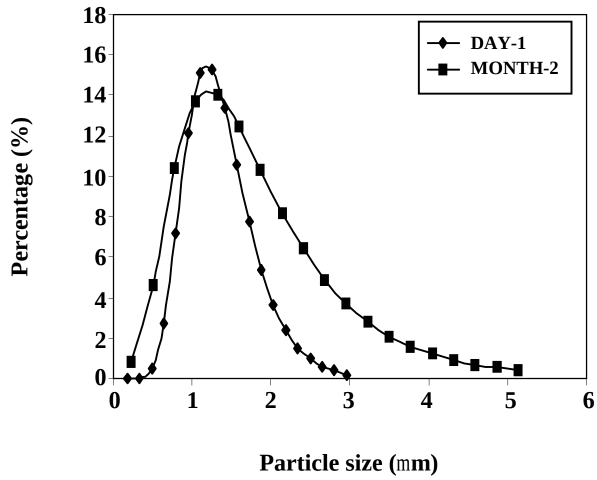


Fig. 4: Particle size distribution in 1 % Barijeh emulsions on the 1st day and two months after preparation at 25 °C .

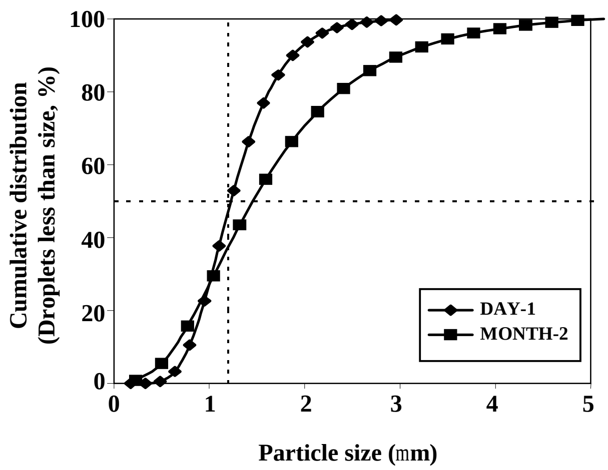
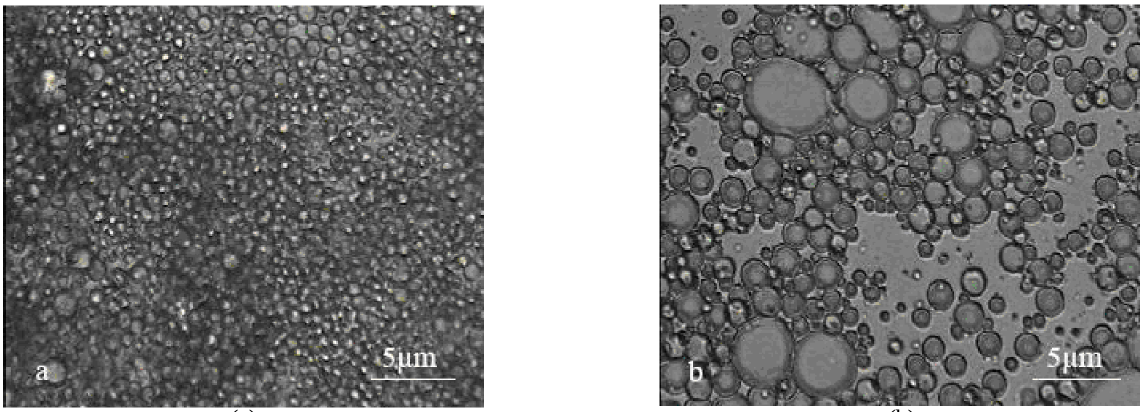


Fig. 5: Cumulative particle size distributions of the 1 % Barijeh gum emulsions on the 1st and after two months storage at 25 °C.



(a) (b)

Fig. 6: Photomicrograph of emulsions prepared with 1% barijeh gum under bright field illumination at the initial state (a) and after two months (b).

adsorption onto the interface (tails or loops) allowing coalescence to occur during the storage stage [18]. After two months of storage, droplet sizes were again larger than those studied after preparation stage indicating coalescence occurring during emulsion aging. Our results showed that emulsions with Barijeh gum have the same droplet size compared to the emulsions prepared with Fenugreek; however, they had smaller droplet size compared to the emulsions prepared with Arabic gum[16].

Light Microscop

The typical micrographs for 1% Barijeh solutions at the initial state and after two months of storage at 25 °C are presented in Fig. 6-a,b and b, respectively. The Barijeh emulsions droplets were small and densely packed and distributed over a narrow size range (Fig. 6-a). After two months of storage, emulsions showed a wide distribution range of particle sizes as smaller droplets started to absorb on the surface of larger droplets (Fig. 6-b). These photos confirmed the results obtained by particle size measurement.

Stability Test

Emulsion stability was observed with respect to creaming and coalescence. In creaming, the emulsion droplets are separated from the continuous phase while moving upwards, depending on the density difference between the continuous and dispersed phases [19]. Coalescence is indicative of emulsion instability, where two or more droplets coalesce to form larger droplets. However, creaming can facilitate coalescence, which results in emulsion breakdown. It is well known that food emulsifiers such as gums are able to produce emulsions of almost unlimited persistence with regards to coalescence [20]. Hence, no attempt was made to study coalescence in this project, and emulsion stability was studied with respect to creaming. It was found that gum concentration significantly influenced the creaming content of emulsions. As shown in Fig. 7, the creaming of emulsions decreased significantly by the increase of gum concentration, but this decrease in the lower concentrations was more important because most of the fat globule surfaces globule surfaces were covered by absorbed gum at the initial state after which, the addition of more gum was not very effective. After two months of storage, creaming volume increased slightly specially at lower concentrations (Fig. 7).

Measurement of Apparent Viscosity

Fig. 8 illustrates the change in the apparent viscosity as a function of shear rate for emulsions with and without 1% gum. The apparent viscosity decreased as the shear rate increased. After a sharp decrease, the viscosity change was smoothened at high shear rates. This might be due to the decrease in the size of colloidal aggregates as the shear rate increases [21].

Although the apparent viscosity of 1% Barijeh emulsions was higher than emulsions without Barijeh, addition of the gum did not have any significant influence on the apparent viscosity. Our results are in agreement with those obtained by *Huang et al.*, (2001) for Arabic gum. The flow behavior of emulsions is related to the colloidal nature of continuous phase as well as the

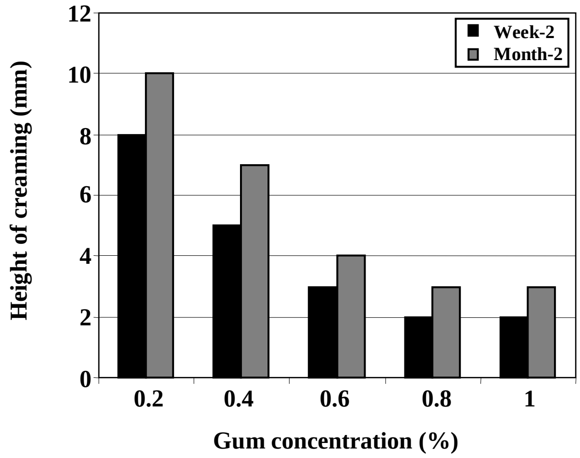


Fig. 7: Height of creaming for emulsions in the presence of various concentrations of gum at the initial state and after two months.

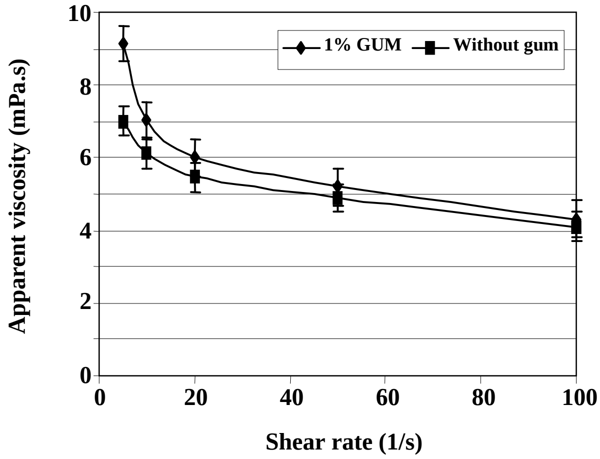


Fig. 8: The change in apparent viscosity of emulsions with and without added gum as function of shear rate.

average particle size and the size distribution. The presence of large molecules such as polysaccharides increased the resistance to flow which, in turn, increased the apparent viscosity of the emulsions but this increase in viscosity wasn't significant.

The stability of emulsions can be attributed to two possible effects: the increase in the viscosity of the dispersed phase and the surface adsorption [22].

Viscosity measurement showed that Barijeh gum increased emulsion viscosity very slightly. The low viscosity of the gum is an important factor when trying to distinguish emulsion stabilization resulting from interfacial adsorption and the viscosity effect that gums can impart on the continuous phase in emulsions.

This gum has high protein content even after purification and seems to be adsorbed on surfaces of oil droplets and reduce surface and interfacial tensions; hence, named as hydrocolloid-emulsifiers. The stabilization seems to be steric (or by a film forming mechanical barrier), due to the weak adsorption of the hydrocolloids onto the oil droplets. This emulsion stabilization mechanism is similar to some hydrocolloids, such as Arabic gum, guar gum, tragacanth gum, and methylcellulose [16, 23-25].

CONCLUSIONS

Results showed that Barijeh gum represents an emulsifying activity, although this was slight especially in more concentrated solutions. This effect was similar to most of the other gums. In addition, emulsion stability after two months was good. Creaming experiments confirmed that emulsion stability in high concentrations of gum was better than low concentrations. Brijeh forms small droplets and stable emulsions at low gum concentrations and seems to have good emulsification ability.

Though further studies are necessary to achieve a more comprehensive characterization of the gum; the properties measured in the present work reveal that it is an interesting potential emulsifying agent for food industry. Therefore, it has been concluded that although Barijeh is basically a polysaccharide, its interfacial and emulsifying properties are derived from its proteineous nature. Additional work is required to pin-point the protein adsorption mechanism and to clarify the role of the protein.

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