Available online at www.sciencedirect.com
SCIENCE DIRECT
Carbohydrate Polymers 65 (2006) 327–336
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

Zeta potential and drop growth of oil in water emulsions stabilized with mesquite gum

J.I. Acedo-Carrillo [a], A. Rosas-Durazo [a], R. Herrera-Urbina [c], M. Rinaudo [d], F.M. Goycoolea [b], M.A. Valdez [a,e,*]

[a] *Departamento de Investigación en Polímeros y Materiales, Universidad de Sonora. Blvd. Transversal y Rosales, Hermosillo, Sonora 83000, Mexico*
[b] *Laboratory of Biopolymers, Centro de Investigación en Alimentación y Desarrollo, A.C. (C.I.A.D., A.C.) P.O. Box 1735 Hermosillo, Sonora 83000, Mexico*
[c] *Departamento de Ingeniería Química, Universidad de Sonora. Blvd. Transversal y Rosales, Hermosillo, Sonora 83000, Mexico*
[d] *Centre de Recherches sur les Macromolécules Végétales, C.N.R.S. affiliated with University Joseph Fourier, B.P. 53, 38041 Grenoble, Cedex 9, France*
[e] *Departamento de Física, Universidad de Sonora. Blvd. Transversal y Rosales, Hermosillo, Sonora 83000, Mexico*

Received 20 November 2004; received in revised form 12 October 2005; accepted 16 January 2006
Available online 28 February 2006

Abstract

The influence of the nature of the oil phase on the zeta potential and the time course evolution of mean droplet-size of emulsions stabilized with mesquite gum have been investigated. Mesquite gum-stabilized emulsions of D-limonene, *n*-decane, *n*-dodecane, *n*-tetradecane *n*-hexadecane, and orange oil were prepared in the range of 9–22% w/w mesquite gum concentrations to investigate the emulsion stability by analyzing creaming, zeta potential, and drop size distribution. An electrosteric mechanism of stabilization is proposed to explain the long term stability observed for orange oil–water emulsions in the range of 9–22% w/w mesquite gum concentrations, similar to the one suggested to operate for gum arabic interfaces. Experiments of creaming for the different emulsions, showed that orange oil–water emulsions observed strong stability in time. By contrast, mesquite gum-stabilized emulsions of D-limonene, *n*-decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane produced less stable emulsions. Light scattering measurements were performed to analyse the Ostwald ripening phenomenon on diluted oil in water emulsions stabilized with mesquite gum of *n*-hexadecane, D-limonene, and orange oil. The averaged hydrodynamic radius showed a linear-like behavior with time except for orange oil drops which kept their size almost constant for more than hundred hours.
© 2006 Elsevier Ltd. All rights reserved.

Keywords: Mesquite gum; Oil in water emulsions; Zeta potential; Light scattering; Ostwald ripening

1. Introduction

Polysaccharides are known to have significantly less surface activity in comparison to proteins (Dickinson & Stainsby, 1988; Garti, Slavin, & Aserin, 1999). This is related to their pronounced hydrophilicity, low flexibility and monotonic repetition of the monomer units in the backbone (Darling & Birkett, 1987). However, if polysaccharides bear auxiliary hydrophobic groups or some proteinaceus moieties attached to their structure, such as highly substituted methylcellulose (Darling & Birkett, 1987), then we obtain some activity at the air–water interface. An example of a successfully modified biopolymer with hydrophobic groups is chitosan (Desbrières, Rinaudo, Babak, & Vikhoreva, 1997). This enhancement of the hydrophobicity leads to improvement of other physical properties of the macromolecule, such as its rheological behavior (Philippova et al., 2001). Recently Garti et al. (1999) have investigated the emulsification capabilities of a polysaccharide gum extracted from *Portulaca oleracea*, which is known to be contaminated by a small amount of proteins. However, up to date it has been very difficult

* Corresponding author. Tel.: +662 2592108; fax: +662 2592109.
E-mail address: valdez@fisica.uson.mx (M.A. Valdez).

0144-8617/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2006.01.016

to find a better natural emulsifier than gum arabic (GA), the bark exudate from *Acacia senegal* and *A. seyal*. This gum is among the most studied and used hydrocolloid worldwide due to its ample spectrum of applications and millenary use.

It has postulated that GA adsorbs at the oil–water interface in the manner shown by Islam, Phillips, Sljivo, Snowden, and Williams (1997), where the arabinogalactan (AG) groups protrude into the solution, while the polypeptide backbone rests at the interface.

Mesquite gum is also a natural polysaccharide exudated by the bark of *Prosopis* spp. trees In previous studies it has been demonstrated that the functionality of mesquite gum is comparable and even superior in certain conditions to that of gum arabic (Beristain, García, & Vernon-Carter, 2001; Beristain, Azuara, & Vernon-Carter, 2002; Beristain & Vernon-Carter, 1994; Goycoolea, Calderón de la Barca, Hernández, Valenzuela, & Balderrama, 2000; Vernon-Carter, Beristain, & Pedroza-Islas, 2000). The Ministry of Health of Mexico has granted authorization for use of mesquite gum in soft drinks, tablets, and feeds.

Chemically, mesquite gum is a highly branched complex proteoglycan. The primary structure of the polysaccharide component has been described in detail (Anderson & Farquhar, 1982; Aspinall & Whitehead, 1970a; Aspinall & Whitehead, 1970b): a central backbone comprised of $\beta(1 \rightarrow 3)$-linked D-galactose residues, to which side oligosaccharide chains of varying size are attached at O(6); these branches contain predominantly D-galactose and L-arabinose (known to occur in both furanose and pyranose forms) and minor proportions of D-glucoronate, 4-*O*-methyl-D-glucuronate, and L-rhamnose. A very similar sugar residue composition is shared by the carbohydrate components of gum arabic from *A. senegal* and other exudate gums from acacia species (Biswas, Biswas, & Phillips, 1995; Defaye & Wong, 1986; Jurasek & Phillips, 1993; Osman, Williams, Menzies, & Phillips, 1993; Street & Anderson, 1983; Stephen, 1990). Besides the carbohydrate components, mesquite gum bears a proteinaceous component that accounts for about 4% of its weight (Goycoolea et al., 2000). Hence mesquite gum can be regarded as an arabinogalactan proteoglycan (AGP) of the Type II (Fincher, Stone, & Clarke, 1983) as gum arabic and related gums. Up to now, the macromolecular structure of mesquite gum has been rationalized as highly branched driving it to a globular disordered conformation in solution. This would account for its high solubility in water and Newtonian rheology even at very high polymer concentration (ca. 50%) (Goycoolea, Morris, Richardson, & Bell, 1995).

Although the overall composition of carbohydrate domains of mesquite gum seems to be closely related to that of gum arabic, both materials can exquisitely be distinguished by different sets of isoantibodies which specifically recognize non-reducing chain termini of the peripheral chains (Miskiel & Pazur, 1991) as well as by crossed immunoelectrophoresis (Goycoolea, Calderón de la Barca, Balderrama, & Valenzuela, 1997). In a recent paper centered on the relation between the macromolecular structure of mesquite gum and its hydrophobic and interfacial properties, it has been suggested that a coiled structure is present for all fractions (López-Franco et al., 2004). In general MG fractions increase the pressure of the air–water monolayer interface much more efficiently than do gum arabic species. In general, mesquite gum (MG) has received much less attention than gum arabic, so that the aim of this paper was to gain further understanding of the emulsifying properties of MG. The role of the nature of the oil phase in MG emulsions was considered an important aspect to address, in line with previous studies conducted on gum arabic (Dickinson, Galzaka, & Anderson, 1991).

The influence of the oil type and emulsifier type on droplet growth in emulsions has been studied recently by Chanami, Horn, and Mc Clements (2002). As they have noticed, gum Arabic has a low interfacial activity and has to be used at much higher concentrations than other types of emulsifier commonly used to stabilize emulsions and the samples vary from batch to batch. Their results indicate too, that in some cases the size of the oil droplets follows a linear dependence with time and others the cubic dependence is the best fit as the oil solubilizes or the interfacial tension increases. Several techniques have been used to analyze the Ostwald ripening phenomenon. The dynamic light scattering (DLS) method and the microscopic conventional method used to measure stability, requires dilution of the samples destroying the organization of the original emulsion (Novales, Papineau, Sire, & Axelos, 2003). However, several investigators have used DLS to directly measure the hydrodynamic radius of non diluted emulsions (Kiokias, Reszka, & Bot, 2004). By reducing the sample thickness to reduce multiple scattering, Lindner, Iritz, and Glatter (2001) have used DLS to measure the hydrodynamic radius of concentrated emulsions by analyzing the structure factor. However, as has been indicated long time ago, multiple scattering must be considered absent for a correct interpretation of the data (Cazabat, Langevin, & Pouchelon, 1980). Some investigators have analyzed the variation of hydrodynamic radius with the volume fraction by using DLS methods (Holmberg, Piculell, Schurtenberger, & Olsson, 2004). In this work, we analyze the evolution in time of the hydrodynamic radius of two different emulsion concentrations by using DLS with different oils (D-limonene, orange oil, *n*-hexadecane) and MG as stabilizer.

On the other hand, one of the studies performed to understand the behavior of hydrocolloids at the oil–water interface is the zeta potential. Several attempts have been done with GA (Jayme, Dunstan, & Gee, 1999) and other hydrocolloids (Garti et al., 1999) where it has been demonstrated the presence of an electrosteric interaction at the oil–water interface due to the macromolecular adsorption.

In the present work, mesquite gum and gum arabic-stabilized emulsions were studied in terms of the stability against creaming and time evolution of the mean oil drop size. Zeta potential measurements by using different oils were performed. To this end, various alkanes hydrocarbon

oils, D-limonene as well as orange essential oil were compared and in some instances, comparisons with GA-stabilized emulsions were established.

2. Experimental

2.1. Materials

Mesquite gum was from a batch obtained from various local suppliers in Hermosillo, Sonora, México. A hand-sorted sample comprising entire, clear, and clean nodules of mesquite gum (classified as "Grade A") was ground in a hammer mill and used throughout this study without any further treatment. Gum arabic was an authenticated sample from *A. senegal* (Ex-Sudan) crude nodules, a gift from Prof. P. Williams of NEWI (Wales, UK). Orange oil was obtained from a Mexican Company (Esencítricos S. de R.L.) and was kept at 8 °C and used as received. D-Limonene, *n*-decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane were of reagent grade, all from Sigma–Aldrich (México). The water used throughout was of 18.3 MΩ cm and obtained from an Easy Pure Instrument from Barnstead.

2.2. Mesquite gum solutions

Mesquite gum (MG) solutions of 9, 15, 17, 20, and 22% w/w were prepared by dissolving the gum by magnetic stirring at room temperature, filtered through Whatman No.1 paper and stored for 24 h at 8 °C.

Emulsions with different oils were prepared by mixing with an Ultra Turrax T25 homogenizer (Janke and Kunkel, Germany) during 4 min at 4000 rev/min. All emulsions were prepared by adding 5 ml oil to 15 ml of MG solution. Hence, the ratios of gum to oil for each of the studied emulsions were 2.7:10, 4.5:10, 5.1:10, 6.0:10, and 6.6:10. Emulsions were used the same day of preparation.

2.3. Particle size

The particle size was measured using a Coulter LS 100 Q instrument, which analyses the intensity of scattered light to produce a particle size distribution, via the Mie theory. We varied the MG concentration of samples and kept some emulsions at 8 °C for 7 days and repeated the particle size measurements to compare the size distribution of the emulsions.

2.4. Emulsification stability index

Emulsification stability index (ESI) is defined as $\mathrm{ESI} = V_7/V_0$, where V_0 and V_7 are the percent by volume of droplets in the range of 2–10 μm, immediately after the emulsion preparation and after 7 days of storage at 8 C (Garti et al., 1999). High ESI numbers indicate better stability to coalescence.

2.5. MG load on emulsion droplets

In order to determine the amount of MG adsorbed at the oil–water interfaces, 20 ml orange oil–water emulsions of 15, 17, 20, and 22% w/w MG concentrations were first centrifuged at 2800*g* for 30 min at 25 °C to separate the oil droplets from the aqueous phase. Serum was then withdrawn with a syringe and the residual MG was obtained by vacuum drying. For the calculation of the mesquite gum content of emulsions, we prepared orange oil–water emulsions with 5, 9, 15, 17, 20, and 22% w/w MG concentrations.

2.6. Creaming

Emulsion stability was evaluated by measuring the extent of gravitational phase separation. This method was used by several authors (Bylaite, Nylander, Venskutonis, & Jönsson, 2001; Flinger, Flinger, & Mangino, 1990) transferring the emulsions into test tubes with an inner diameter of 5.7 mm and length of 22 cm. Tubes were capped and stored at room temperature. The creamed process was registered by measuring the serum layer height in the test tube.

2.7. Time dependence of hydrodynamic radius

DLS measurements were performed using an ALV - 5000 digital correlator system (Langen-GmbH, Germany) fitted with a temperature control set at 25 ± 0.1 °C. The scattered light, vertically polarized with a $\lambda_0 = 632$ nm argon laser (30 mW), was measured at 90°, the refractive index was measured with a refractometer (Mettler-Toledo, model RE4OD). The hydrodynamic radius, R_H, was obtained for diluted samples from the Stokes–Einstein relation

$$D_0 = \frac{k_B T}{6\pi\eta R_H}, \quad (1)$$

where k_B is the Boltzmann constant, T is the absolute temperature D_0 is the diffusion coefficient and η the viscosity of the solvent.

The solvent and emulsions for hydrodynamic radius measurements at different times were prepared as follows.

Solvent was prepared as phosphate buffer solution (20.7 g dibasic sodium phosphate and 1.691 g monobasic sodium phosphate diluted in 1 L Milli Q water). Sodium azide (0.1% wt) was added as bactericide. *n*-Hexadecane, D-limonene, and orange oil were mixed with mesquite gum solutions and D-limonene with gum Arabic. Two different concentrations of oil in water emulsions were produced. The most concentrated emulsions were produced by mixing 0.5 ml oil and 9.5 ml mesquite or gum Arabic 1% wt solutions. Emulsions were homogenized with the same instrument described above at 8000 rpm for 1 min. Diluted emulsions were produced by adding and gently mixing 1.5 ml solvent with 1.5 ml of the original emulsions

to get a volume fraction of 0.025. All solutions were kept at room temperature in capped cells used for light scattering and gently agitated before each measurement. Averaged measurements were obtained with three runs of 30 s each.

2.8. Zeta potential measurements

For the measurements of zeta potential for different pH and salt concentrations, we picked up a drop of an oil–water emulsion stabilized with 9% w/w MG and dissolved it in 100 ml milli Q water. For all the measurements, we added to the water 0.001 M $NaNO_3$ to fix the ionic strength. Two different NaCl salt concentrations were used: 0.001 and 0.01 M. pH was adjusted with 0.1 M solutions of HNO_3 and NaOH; finally the suspension was conditioned for 20 min before used to measure zeta potential or the size of particles.

Zeta potential was measured with a Zeta-Meter 3+ unit (Zeta Meter, Inc., New York). This apparatus includes a microprocessor that first measures the electrophoretic mobility of colloidal particles dispersed in aqueous solutions, and then automatically calculates the zeta potential using the Smoluchowski equation. The values obtained are average values obtained by tracking at least 20 different particles. The average deviations of the measurements were less than 5%.

3. Results

In the present study, the droplet diameter from different emulsions prepared with varying oil phases, namely *n*-alkanes of varying chain length, D-limonene and orange oil were measured by using 15 w/w% MG concentration. Emulsions were produced at 4000 rpm for 4 min and the Coulter instrument was used as described before. It was observed that the mean diameter of droplets of *n*-decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane immediately after preparation was in the range of 4–4.5 μm. For the case of orange oil, we found an average diameter ranging from 2.5 to 3.0 μm. A small variation of the mean diameter after 1 week for orange o/w emulsions containing 15, 17, 20, and 22% w/w MG concentrations was noticed; however the standard deviations resulted high, so that the effect can be considered as negligible. The behavior observed for all alkanes was similar without showing any important change in the droplet mean diameter after a week. For the case of D-limonene, we obtained an increase of the mean droplet size after 1 week, as observed in Table 1. We calculated the average area of the orange oil in the emulsions and compared it with the area of the D-limonene after a week and found that orange oil covered two times more area than D-limonene. This is probably due to the affinity of MG molecules with the orange oil–water interface (Bylaite et al., 2001) and, as pointed out by Buffo and Reineccius (2001), to the Ostwald ripening process which can be increased with essential oils somewhat soluble in water (Dickinson, 1986).

Table 1
Average droplet diameter and emulsion stability index (ESI) of different oil droplets of oil in water emulsions stabilized with 15% w/w MG concentration, measured immediately after emulsion preparations (day 1) and after a week (day 7)

Oil phase	Diameter (μm)[a] day 1	Diameter (μm)[a] day 7	ESI
Orange oil	2.5 (2.0)	2.3 (1.5)	0.98
D-Limonene	3.2 (2.0)	6.0 (2.0)	0.53
n-Decane	4.0 (1.8)	3.6 (1.7)	0.98
n-Dodecane	4.0 (2.0)	3.5 (1.7)	0.97
n-Tetradecane	4.3 (2.0)	5.0 (1.8)	0.95
n-Hexadecane	4.5 (1.6)	5.0 (1.6)	0.93

[a] Mean values and standard deviation (in brackets) of triplicate analysis.

ESI results for orange o/w emulsions containing 15, 17, 20 and 22% w/w MG revealed a low tendency to coalesce in all cases and the ESI values were in the range (0.80–0.98). For the case of the other oils used, as observed in Table 1, only D-limonene decreased significantly its ESI.

The influence of the nature of the oil phase on the emulsifying behavior of gum arabic has been investigated by Dickinson et al. (1991). They reported the time dependence of droplet-size distribution of oil in water emulsions made with *n*-hexadecane, D-limonene, and orange oil and found a different tendency of droplets coalescence between *n*-hexadecane on the one hand and D-limonene and orange oil on the other, caused principally by the Ostwald ripening process (Dickinson, 1986). In our case, emulsions prepared with the first homogenization method (4000 rpm), MG and D-limonene showed evidences of the Ostwald ripening process as can be observed in Fig. 1a. In Figs. 1a and b, we show the oil drops distribution of D-limonene and orange oil emulsions stabilized with 15% wt MG an hour and 7 days after the emulsions preparation. The differences of these two oil drop distributions with time were evident and we decided to analyze the drop behavior with the DLS method.

The time dependence of the droplet size distribution of different emulsions were measured with the DLS method as described in the experimental part. The results are shown in Figs. 2a and b, where the behavior of R_H is shown for different times. In Fig. 2a, we show the behavior for R_H for an oil volume fraction of 0.05. The behavior of the droplet size for D-limonene emulsions stabilized with MG showed a higher rate of change with time as compared with the corresponding one stabilized with gum arabic. It is interesting to notice that the average diameter obtained resulted smaller as the ones shown in Table 1 for the same emulsions homogenized at lower revolutions and higher concentrations of MG and gum arabic. Notice however, that orange oil droplets remain almost without change in time as observed for emulsions at higher concentrations. This behavior of MG on the orange oil emulsions to stop or control Ostwald ripening can be explained, among other arguments, due to the fact that orange oil is less water soluble than D-limonene. The control of the Ostwald ripening process was demonstrated by Welin-Berger and Bergenstahl

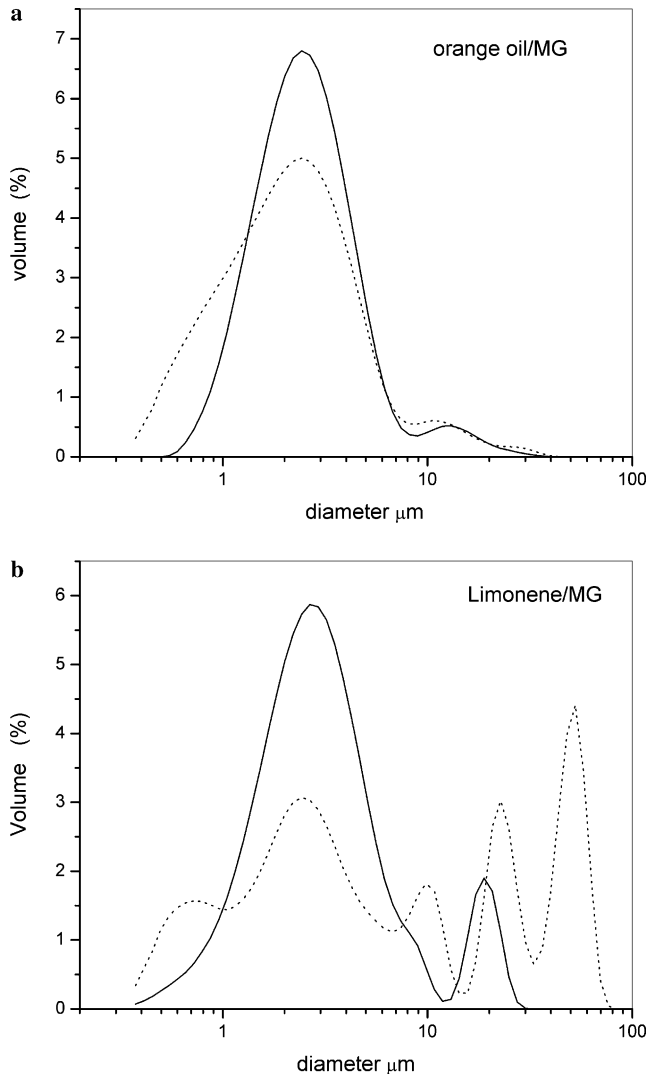

Fig. 1. Particle size distribution of orange oil and D-limonene emulsions stabilized with 15% wt MG solutions measured with a Coulter LS 100 Q instrument. Solid lines correspond to measurements an hour after emulsions preparation and dotted curves correspond to drop size distributions measured 7 days after emulsions preparation. The oil volume fraction used was 0.25. (a) Orange oil–water emulsions, (b) D-limonene–water emulsions.

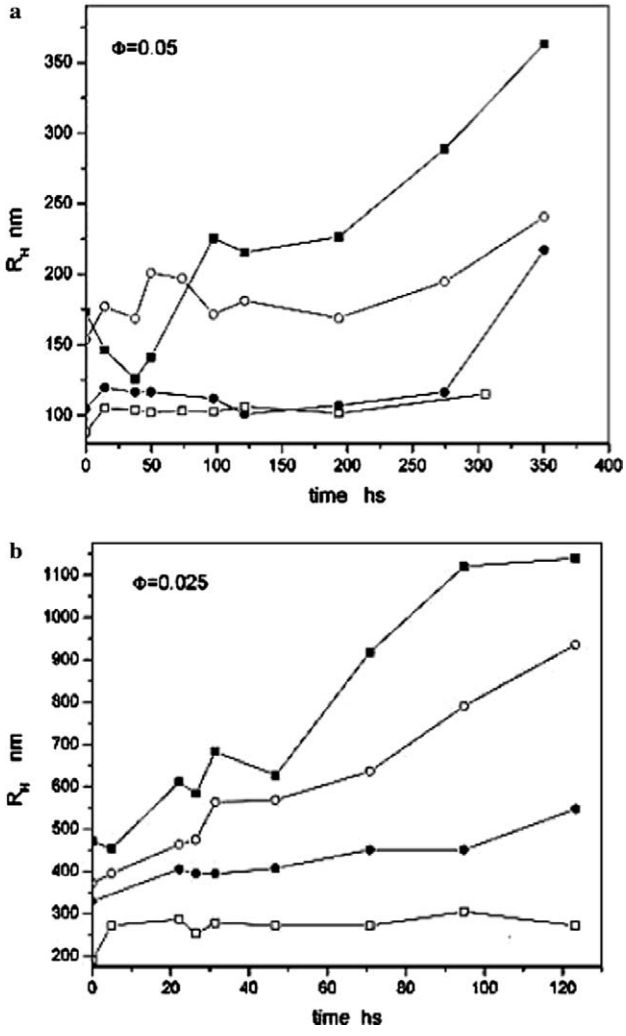

Fig. 2. Time evolution of the average hydrodynamic radius of diluted o/w emulsions, measured with the ALV -5000 digital correlator system. Orange oil (open squares), D-limonene (filled squares) and hexadecane (open circles) emulsions were stabilized with 1% (w/w) MG. D-Limonene emulsions (filled circles) were stabilized with 1% (w/w) gum arabic. (a) $\Phi = 0.05$ oil volume fraction and (b) $\Phi = 0.025$ oil volume fraction.

(2000) by adding a less soluble oil to their emulsions producing stable oil drops for long time. Alternatively, any increase of the viscosity of the emulsion due to an increase in the effective volume fraction of the present droplets as a result of either attractive or repulsive forces, can result in a sol–gel transition and will also contribute to arrest Ostwald ripening. In an accompanying paper (Valdez et al., 2006), evidence is given that MG-stabilized orange oil emulsions do exhibit a true liquid–solid rheological transition.

The time dependence of the diluted solutions obtained at the volume fraction 0.025 is shown in Fig. 2b. Notice that almost all emulsions showed a linear-like behavior, except again in the case of orange oil which shows an almost constant R_H value. Chanami et al. (2002) have also obtained in some cases a linear behavior for some emulsifiers and different oil types and in others, a cubic behavior of R_H with time when the oil solubilizes.

In Fig. 3, we show the first and the last drop size distributions for orange oil and D-limonene ($\Phi = 0.025$), both stabilized with MG. We observe a broader distribution for the case of D-limonene droplets similar to the droplet distribution found by Dickinson (1986). In the case of orange oil droplets, we notice a sharper distribution and the particle size range does not seem to change significantly after more than 100 h. This behavior was also observed with the Coulter instrument for more concentrated orange oil emulsions, where the ESI index showed values around 98% indicating great stability with time.

The aging effect of MG emulsions is shown for three different oils in Fig. 4. It was noticed that for D-limonene

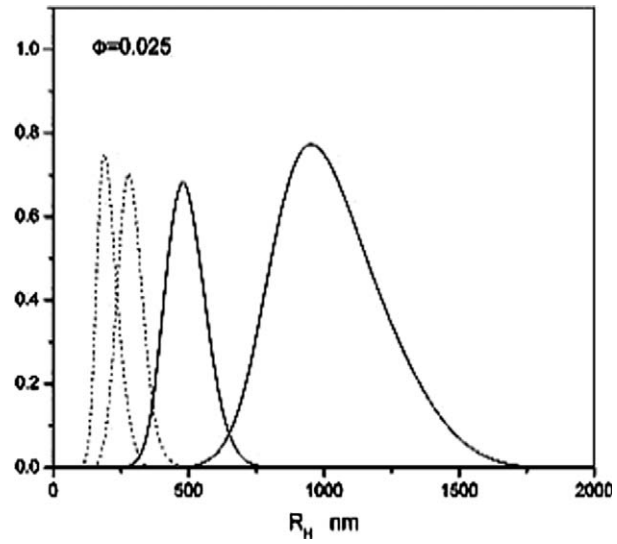

Fig. 3. Particle size distribution of orange oil and D-limonene emulsions stabilized with 1% wt MG solutions measured with the ALV-5000 digital correlator instrument. Solid lines correspond to D-limonene emulsions an hour and 120 h after the emulsion preparation; dotted curves correspond to orange oil emulsions measured at the same times. The oil volume fraction used was 0.025.

and *n*-decane, phase separation starts within the first 24 h after preparation and this process practically ends in 7 days. For the case of orange oil on the contrary, the formation of the creamed phase is slower, specially for the 20 and 22% w/w MG concentration. These aging time differences between orange oil and the other oils (alkanes and D-limonene) can be explained (among others) due to the larger particle size of the oil droplets of alkanes and D-limonene with respect to orange oil, to the oil density differences and to the greater viscosity of orange oil emulsions (Bylaite et al., 2001; Buffo, Reineccius, & Ochlert, 2001). Finally it deserves to mention, that, at the same concentration range, gum arabic emulsions showed a similar aging time behavior as the one observed for MG by using D-limonene and *n*-decane. This corroborates the observations of Chanami et al. (2002), indicating the need of larger gum Arabic concentrations to stabilize emulsions.

MG load on o/w emulsions droplets for orange oil and increasing MG concentrations is shown in Fig. 5. The values in the y axis indicate the amount of MG retained in the emulsion after phase-separation by centrifugation and analysis of the liquid phase as a function of varying amounts of MG in the solution. We observed that for the sample prepared with 22% w/w MG, virtually no phase separation was noticed and the whole MG is almost completely retained in the creamed phase. This result is in agreement with the time course stability experiment observed at this same concentration (Fig. 4c). However, the typical protein concentrations found by other authors are lower (Buffo et al., 2001; Garti et al., 1999). This could indicate that MG at the orange oil–water interface build

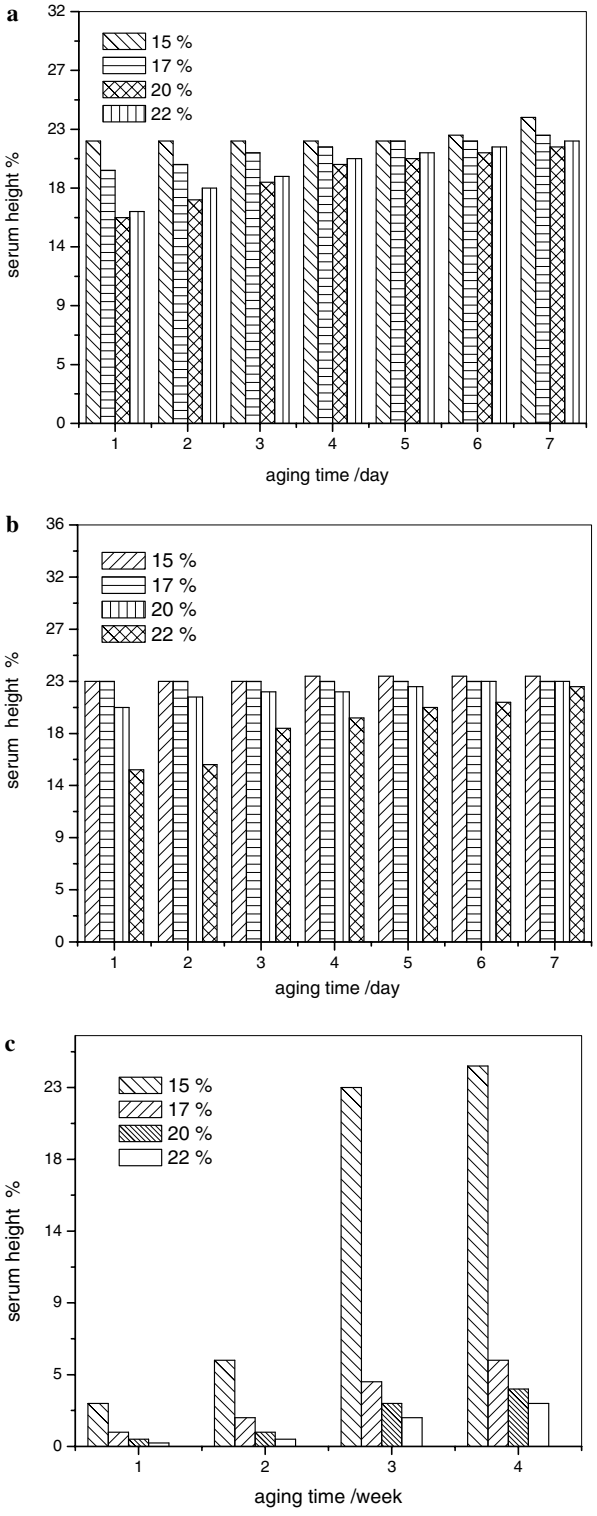

Fig. 4. Aging time of oil in water emulsions for different MG concentrations and different oils at pH 7. The height in the *y*-axis corresponds to the serum layer in%. (a) D-Limonene, (b) *n*-decane, and (c) orange oil.

more complex structures than simple monolayers and hence the involved molecular species can be joined to form aggregates and possibly a gel network as we deduce from the rheological measurements (Valdez et al., 2006).

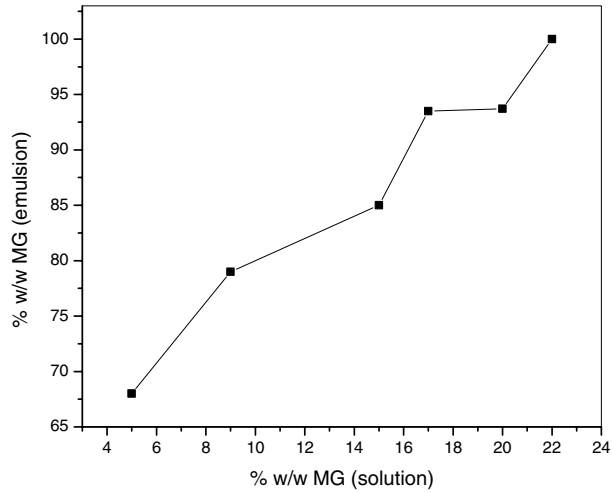

Fig. 5. MG load on oil–water emulsions for orange oil and increasing MG concentrations at pH 7.

3.1. Zeta potential

Our calculations of zeta potential were performed by using the Smoluchowski equation without taking into account any other approach. This was done due to the fact that the particle size of our emulsions is relative large and that the electrokinetic radius, ka, (k is the inverse of the Debye length and a the drop radius) resulted larger than 400. According to the results of Moncho, Martínez-López, and Hidalgo-Álvarez (2001), at this limit, the approaches of O'Brien and White (1978) and Dukhin (1995) converge to the Smoluchowski equation, so that differences are expected to be small.

The effect of pH at different NaCl concentrations for orange oil in water 9% w/w MG emulsions on the zeta potential is illustrated in Fig. 6. As it is noticed, an increase in pH results in accompanied by an increase in zeta potential values magnitude reaching an approximated constant

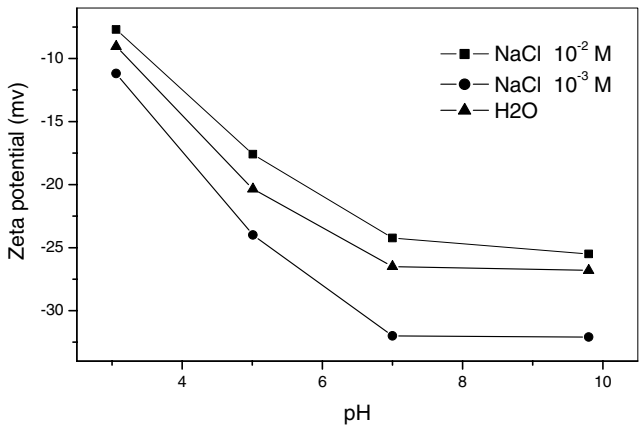

Fig. 6. Zeta potential of orange oil–water emulsions stabilized with 9% w/w MG versus pH at different NaCl concentrations. The water contained 0.001 M $NaNO_3$ to fix the ionic strength. (triangles) water, (circles) 10^{-3} M NaCl, (squares), and 10^{-2} M NaCl.

value at pH around 7 in all cases. We observed that as the NaCl concentration rises from 10^{-3} to 10^{-2} M NaCl, leading to a compressed electrical double layer, the repulsion is reduced obtaining comparatively low zeta potential values at all pHs. Similar behavior was observed for gum arabic by Jayme et al. (1999) and for other hydrocolloids (Garti et al., 1999). This similar behavior of gum arabic and mesquite gum could be a consequence of the presence of protein–polysaccharide complexes in both samples and as demonstrated by these authors, the mechanism by which both gums stabilizes microemulsions is electrosteric rather than of purely steric or electrostatic. This means that stabilization arises from the mutual repulsion between the electrical double layer of particles and from the adsorption of macromolecules at the oil drops. The calculated zeta potential values ranged from -24 for 10^{-2} M NaCl to -32 mV for 10^{-3} M NaCl at pH > 7. These values are near to the one reported by Anderson (1988), who found a value of -20 mV for a 10^{-2} M NaCl in gum arabic emulsions and to the one reported by Jayme et al. (1999) around -25 mV for a 10^{-2} M NaCl solution.

Anderson (1988) has explained the inadequacy of the DLVO approach to understand the emulsions stability according to his zeta potential measurements. The DLVO model shows that the positive primary maximum in the potential plot, serving as the energy barrier to the irreversible flocculation, should to be $>1.5kT$ (>37.5 mV) at room temperature to prevent particle contact and produce a metastable system (Ingersen, Klein, & Pincus, 1990). As observed in Fig. 6 for all salt concentrations and pH used, according to this model, an irreversible flocculation should occur. Due to the protein content of mesquite gum, similar to the protein content of gum arabic (López-Franco et al., 2004), we assume that the polypeptide chains remain attached to the oil surface and the polysaccharide tails stay in the water phase producing the net charge at the oil surface and along with the steric (repulsive) effect it contributes to the emulsion stability.

Zeta potential of o/w MG-stabilized emulsions using both D-limonene and orange oil at varying MG concentrations is shown in Fig. 7. As observed, the behavior of the emulsions is different and depends strongly on the oil and the MG concentration used. Emulsions containing D-limonene attained much larger zeta potential values Even when D-limonene is known to be the major component of orange oil, there are differences in chemical composition between both oils as evidenced by FTIR spectroscopy (results not shown). These differences may suggest a very specific interaction between components of MG and orange essential oil other than D-limonenene (e.g., terpenes, among other). Fatty acids and other impurities present in orange oil may also play a role in the zeta potential behavior.

As observed in Fig. 7, for the orange oil emulsion and highest concentration used (22% w/w), the zeta potential value is close to the energy barrier obtained from the DLVO model by Anderson (1988) to explain the flocculation phenomenon of microemulsions. We conclude that,

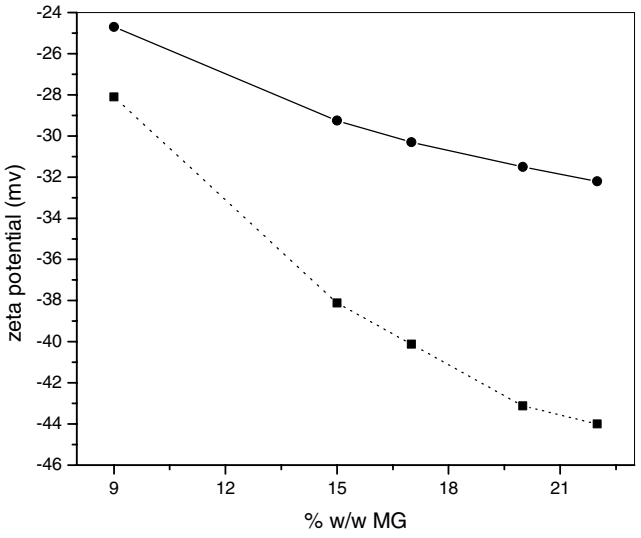

Fig. 7. Zeta potential of emulsions with different MG concentrations at pH 7 for two different oils: orange oil (solid curve), D-limonene (dotted curve).

in spite of the fact that zeta potential values of MG emulsions prepared with D-limonene resulted higher than the ones obtained by using orange oil, the orange oil emulsions showed longer stability due probably to a different steric interaction, to the different chemical compositions of the used oils, different oil drop sizes or to differences in viscosity.

Zeta potential of emulsions of aliphatic hydrocarbons in water, stabilized with 15% w/w MG at the pH of water (~6.1), were also measured to observe the influence of the chain size of the emulsified oil. In Fig. 8, we observe the results for 10, 12, 14, and 16 carbons in the aliphatic chain at fixed MG concentration. We notice that zeta potential decreases slightly in magnitude when the chain size increases (−44 to −36 mV). This variation is very reduced, taking account that the error bars are around 5% (not shown). Comparing our results with the ones of Stachurski and Michalek (1996), for the same hydrocarbons and pH 6 (around −80 mv), we observe a drastic reduction of the magnitude of the zeta potential due to the presence of the MG at the oil–water interface. Stachurski and Michalek (1996) found that from 9 to 16 carbons in the chain, the zeta potential varies slightly on the hydrocarbon length as pH of the aqueous solutions was varied. They claim that the origin of the negative value of the zeta potential of hydrocarbon droplets is caused by a selective adsorption of $^{-}$OH ions which makes the excess of negative charge to build up at the oil–water interface. In our case, the protein–polysaccharides complexes substitute the $^{-}$OH at the oil–water interface due probably to the more strong non-polar interactions established between non-polar polypeptides and hydrocarbons than that between hydrocarbons and the $^{-}$OH molecules and therefore the obtained values are similar to the ones obtained when orange oil or D-limonene were used (Fig. 7).

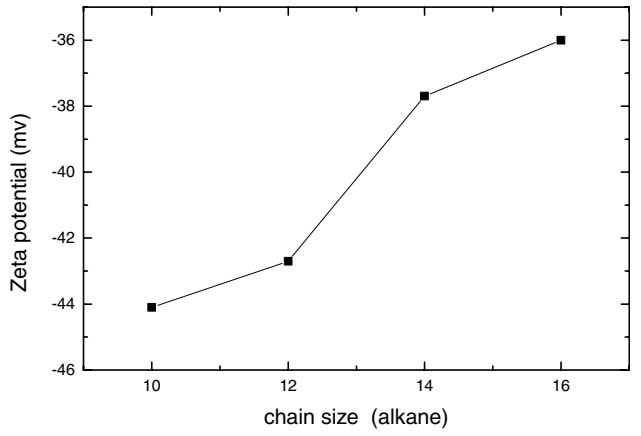

Fig. 8. Zeta potential of oil in water emulsions with different chain length of different alkanes in the oil phase, fixing pH (7), and MG concentration (15% w/w).

4. Conclusions

In this work, we have investigated the influence of different oils (D-limonene, *n*-decane, *n*-dodecane, *n*-tetradecane, *n*-hexadecane, and orange oil) on the stability and elektrokinetic behavior of mesquite gum-stabilized oil in water emulsions.

The time evolution pattern of the growth of the particle size showed that orange oil emulsions were more stable against gravitational separation and coalescence than the emulsions obtained with the other oils when mesquite gum was used as stabilizer. Different oils tested, other than orange oil, showed an Ostwald ripening-like behavior for both mesquite gum and gum Arabic-stabilized emulsions. By contrast, orange oil drops maintained their smaller average size for longer times, probably due to a strong electrosteric interaction similar to the one mediating in gum Arabic emulsions. This strong interaction observed for mesquite gum and orange oil, as probed by zeta potential measurements, originates a large mesquite gum load at the oil–water interface, a condition that results in a gel-like behavior at low mesquite gum concentrations, a phenomenon that is not observed for Gum Arabic.

Acknowledgements

El Consejo Nacional de Ciencia y Tecnología (CONACYT, México) is gratefully acknowledged for Grant No. SEP-2004-C01-46749, for the scholarship of one of the participants (J.I. Acedo-Carrillo) and for the financial support to get possible the stage of Dra. M. Rinaudo in Hermosillo, Sonora, México. We also thank CIAD, A.C. (Centro de Investigación para la Alimentación y Desarrollo) and the Universidad de Sonora where this work was done.

References

Anderson, D. M. W. (1988). The current toxicological status of permitted emulsifiers and stabilizers. In G. O. Phillips, D. J. Wedlock, & P. A.

Williams (Eds.). *Gums and stabilizers for the food industry* (Vol. 4, pp. 417–424). Washington, DC: IRL Press.

Anderson, D. M. W., & Farquhar, G. K. (1982). Gum exudates from the genus *Prosopis*. *The International Tree Crops Journal, 2*, 15–24.

Aspinall, G. O., & Whitehead, C. C. (1970a). Mesquite gum. I. The 4-*O*-methylglucuronogalactan core. *Canadian Journal of Chemistry, 48*, 3850–3855.

Aspinall, G. O., & Whitehead, C. C. (1970b). Mesquite gum. II. The arabinan peripheral chains. *Canandian Journal of Chemistry, 48*, 3840–3849.

Beristain, C. I., García, H. S., & Vernon-Carter, J. E. (2001). Spray-dried encapsulation of cardamom (*Elettaria cardamomum*) essential oil with mesquite (*Prosopis juliflora*) gum. *Lebensmittel Wissenschaft und Technologie, 34*, 398–401.

Beristain, C. I., Azuara, E., & Vernon-Carter, J. E. (2002). Effect of water activity on the stability to oxidation of spray-dried encapsulated orange peel oil using mesquite gum (*Prosopis juliflora*) as wall material. *Journal of Food Science, 67*, 206–211.

Beristain, C. I., & Vernon-Carter, J. E. (1994). Determination of moisture desorption enthalpy of mesquite gum with differential scanning calorimetry and thermogravimetric analysis. *Drying Technology, 12*, 727–733.

Biswas, S., Biswas, B., & Phillips, G. O. (1995). Classification of natural gums. Part VIII. Chemometric assignment of commercial gum exudates from Africa using cluster analysis on the protein amino acid compositions. *Food Hydrocolloids, 9*, 151–163.

Buffo, R. A., & Reineccius, G. A. (2001). Shelf-life and mechanisms of destabilization in dilute beverage emulsions. *Flavour and Fragrance Journal, 16*, 7–12.

Buffo, R. A., Reineccius, G. A., & Ochlert, G. W. (2001). Factors affecting the emulsifying and rheological properties of gum acacia in beverage emulsions. *Food Hydrocolloids, 15*, 53–66.

Bylaite, E., Nylander, T., Venskutonis, R., & Jönsson, B. (2001). Emulsification of carway essential oil in water by lecithin and β lactoglobulin: Emulsion stability and properties of the formed oil aqueous interface. *Colloids and Surfaces B: Biointerfaces, 20*, 327–340.

Cazabat, A. M., Langevin, D., & Pouchelon, A. (1980). Light scattering study of water–oil microemulsions. *Journal of Colloid and Interface science, 73*, 1–12.

Chanami, R., Horn, G., & Mc Clements, D. J. (2002). Influence of oil polarity of droplet growth in oil in water emulsions stabilized by a weakly adsorbing biopolymer or nonionic surfactant. *Journal of Colloid and Interface Science, 247*, 167–176.

Darling, D. F., & Birkett, R. J. (1987). Food hydrocolloids in practice. In E. Dickinson (Ed.), *Food emulsions and foams* (pp. 1–29). London: Royal Society of Chemistry.

Defaye, J., & Wong, E. (1986). Structural studies of gum arabic. The exudate polysaccharide from *Acacia senegal*. *Carbohydrate Research, 150*, 221–231.

Desbrières, J., Rinaudo, M., Babak, V., & Vikhoreva, G. (1997). Surface activity of water soluble amphiphilic chitin derivatives. *Polymer Bulletin, 39*, 209–215.

Dickinson, E., & Stainsby, G. (1988). Emulsion stability. In E. Dickinson & G. Stainsby (Eds.), *Advances in food emulsions and foams* (pp. 1–44). Essex: Elsevier Applied Science.

Dickinson, E., Galzaka, V. B., & Anderson, D. M. W. (1991). Emulsification behaviour of gum arabic: Part 1: effect of the nature of the oil phase on the emulsion droplet size distribution. *Carbohydrate Polymers, 14*, 373–383.

Dickinson, E. (1986). Emulsions. In *Annual Reports in the Progress of Chemistry* (pp. 31–58). London: Royal Society of Chemistry.

Dukhin, S. S. (1995). Electrochemical characterization of the surface of a small particle and nonequilibrium electric surface phenomena. *Advances in Colloid and Interface Science, 61*, 17–49.

Fincher, G. B., Stone, B. A., & Clarke, A. E. (1983). Arabinogalactan-proteins: structure, biosynthesis, and function. *Annual Review in Plant Physiology, 34*, 47–70.

Flinger, K. L., Flinger, M. A., & Mangino, M. E. (1990). The effects of compositional factors on the short-term physical stability of a concentrated infant formula. *Food Hydrocolloids, 4*, 95–104.

Garti, N., Slavin, Y., & Aserin, A. (1999). Surface and emulsification properties of a new gum extracted from Portulaca Oleracea. *Food Hydrocolloids, 13*, 145–155.

Goycoolea, F. M., Calderón de la Barca, A. M., Hernández, G., Valenzuela, J. R., & Balderrama, J. R. (2000). Immunochemical, structural and functional properties of mesquite gum in comparison with gum arabic. In E. A. Nothnagel, A. E. Clarke, & A. Bacic (Eds.), *Cell and developmental biology of arabinogalactan-proteins* (pp. 263–276). New York: Kluwer Academic/Plenum Publishers.

Goycoolea, F. M., Morris, E. R., Richardson, R. K., & Bell, A. E. (1995). Solution rheology of mesquite gum in comparison with gum arabic. *Carbohydrate Polymers, 27*, 37–45.

Goycoolea, F. M., Calderón de la Barca, A. M., Balderrama, J. R., & Valenzuela, J. R. (1997). Immunological and functional properties of the exudates gum from northwestern Mexican mesquite (*prosopis* spp.) in comparison with gum Arabic. *International Journal of Biological Macromolecules, 21*, 29–36.

Holmberg, A., Piculell, L., Schurtenberger, P., & Olsson, U. (2004). Oil continuous microemulsions mixed with an amphiphilic graft copolymer or with the parent homopolymer. Polymer droplet interactions as revealed by phase behavior and light scattering. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 250*, 325–336.

Ingersen, K., Klein, J., & Pincus, P. (1990). Forces between surfaces and adsorbed polymers 3. θ solvent. Calculations and comparison with experiment. *Macromolecules, 23*, 548.

Islam, A. M., Phillips, G. O., Sljivo, A., Snowden, M. J., & Williams, P. A. (1997). A review of recent developments on the regulatory, structural and functional aspects of gum arabic. *Food Hydrocolloids, 11*, 493–505.

Jayme, L., Dunstan, D. E., & Gee, M. L. (1999). Zeta potentials of gum arabic stabilized oil in water emulsions. *Food Hydrocolloids, 13*, 459–465.

Jurasek, P., & Phillips, G. O. (1993). The classification of natural gums. Part IV. Identification and discrimination of Acacia, Combretum and Prosopis gum exudates. *Food Hydrocolloids, 7*, 337–352.

Kiokias, S., Reszka, A. A., & Bot, A. (2004). The use of static light scattering and pulse-field gradient NMR to measure droplet sizes in heat-treated acidified protein-stabilized oil in water emulsion gels. *International Dairy Journal, 14*, 287–295.

Lindner, H., Iritz, G., & Glatter, O. (2001). Measurements on concentrated oil in water emulsions using static light scattering. *Journal of Colloid and Interface Science, 242*, 239–246.

López-Franco, Y. L., Valdez, M. A., Lizardi, J., Hernández, J., Calderón de la Barca, A. M., Rinaudo, M., et al. (2004). Macromolecular dimensions and mechanical properties of monolayer films of Sonorean mesquite gum. *Macromolecular Bioscience, 4*, 865–874.

Miskiel, F. J., & Pazur, J. H. (1991). The preparation and characterization of antibodies with specificity for the carbohydrate units of gum arabic and gum mesquite. *Carbohydrate Polymers, 16*, 17–35.

Moncho, A., Martínez-López, F., & Hidalgo-Álvarez, R. (2001). Comparative study of theories of conversion of electrophoretic mobility into ς potential. *Colloids and Surfaces: A: Physicochemical and Engineering Aspects, 192*, 215–226.

Novales, B., Papineau, P., Sire, A., & Axelos, M. A. V. (2003). Characterization of emulsions and suspensions by video image analysis. *Colloids and Surfaces A: Physicochemical Engineering Aspects, 221*, 81–89.

O'Brien, R. W., & White, L. R. (1978). Electrophoretic mobility of a spherical colloidal particle. *Journal of Chemical Society Faraday Transactions, 2/77*, 1607–1626.

Osman, M. E., Williams, P. A., Menzies, A. R., & Phillips, G. O. (1993). Characterization of commercial samples of gum arabic. *Journal of Agricultural and Food Chemistry, 41*, 71–77.

Philippova, O. E., Volkov, E. V., Sitnikova, N. L., Khokhlov, A. R., Desbrieres, J., & Rinaudo, M. (2001). Two types of hydrophobic

aggregates in aqueous solutions of chitosan and its hydrophobic derivative. *Biomacromolecules, 2*, 483–490.

Street, C. A., & Anderson, D. M. W. (1983). Refinement of structures previously proposed for gum arabic and other Acacia gum exudates. *Talanta, 30*, 887–893.

Stephen, A. M. (1990). Structure and properties of exudate gums. In G. O. Phillips, P. A. Williams, & D. J. Wedlock (Eds.), *Gums and stabilisers for the food industry* (pp. 3–16). IRL Press on Oxford University.

Stachurski, J., & Michalek, M. (1996). The effect of the ς potential on the stability of a non polar oil-in water emulsion. *Journal of Colloid and Interface Science, 184*, 433–436.

Valdez M. A., Acedo-Carrillo, J. I., Rosas-Durazo, A., Lizardi, J., Rinaudo, M., & Goycoolea F. M. (2006). Small-deformation rheology of mesquite gum stabilized oil in water emulsions, *Carbohydrate Polymers*, (in press).

Vernon-Carter, J. E., Beristain, C. I., & Pedroza-Islas, R. (2000). Mesquite gum (*Prosopis gum*). In G. Doxastakis & V. Kiosseoglou (Eds.). *Novel macromolecules in food systems, developments in food science* (Vol. 41, pp. 217–238). The Netherlands: Elsevier.

Welin-Berger, K., & Bergenstahl, B. (2000). Inhibition of Ostwald ripening in local anesthetic emulsions by using hydrophobic excipients in the disperse phase. *International Journal of Pharmaceutics, 200*, 249–260.