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Small-deformation rheology of mesquite gum stabilized oil in water emulsions

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Abstract

The influence of the nature of the oil phase on the viscoelastic properties of emulsions stabilized with mesquite gum has been investigated. Mesquite gum-stabilized emulsions of D-limonene, *n*-decane, *n*-dodecane, *n*-tetradecane *n*-hexadecane and orange oil were analyzed, the observations showed that the nature of the oil used was determinant for the viscoelastic and gel formation ability of the emulsions. Orange oil-in-water emulsions stabilized with mesquite gum developed a gel-like structure with time, in contrast to the emulsions obtained with alkane oils and with D-limonene. This is rationalized in terms of a weak gel network of protein-polysaccharides molecules interconnecting spherical oil droplets. The gelling behavior of these systems has been described with a model derived from percolation theory.

Keywords: Mesquite gum; Oil in water emulsions; Rheology; Gel

1. Introduction

The rheological properties of emulsions have been investigated from both the theoretical and the practical standpoint. In very dilute emulsions stabilized by nonionic surfactants or proteins as long as the droplets are completely dispersed, the viscosity of dilute nonaggregated emulsion systems has been described by the well-known Einstein equation (Buffo & Reineccius, 2002; Dickinson and McClements, 1996). As emulsions become more concentrated, their viscoelastic properties become more apparent. In fact, the mechanical properties of highly concentrated emulsions (with volume fractions ≥ 0.9) have much more in common with foams. The rheology of such systems is largely determined by the thin liquid film between the droplets (Dickinson and McClements, 1996). In flocculated protein-stabilized systems, it has been observed that the main contribution to the shear modulus comes from micro-gel formation involving adsorbed macromolecules on neighboring emulsions droplets. It has also been known for decades that gum arabic forms cohesive and elastic films at the air–water and especially so at air–oil interfaces and the time-dependent thickening behavior has been studied using small-amplitude oscillatory rheological tests (Sanchez, Renard, Robert, Schmitt, & Lefebvre, 2002). In a recent study, a conventional rheometer has been modified so as to study the interfacial shear viscosity and interfacial viscoelastic properties of mesquite mixed with oppositely charged chitosan, an aminoglycan, at the oil–water interface using mineral oil.

The role of the nature of the oil phase on the thermodynamic stability of emulsions stabilized by MG or gum arabic and on their electrical properties (zeta potential) has been addressed in an accompanying paper (Acedo-Carrillo, Rosas-Durazo, Herrera-Urbina, Rinaudo, Goycoolea, & Valdez, accepted 2006). It was firmly demonstrated that the droplet size of MG-stabilized emulsions of orange deterpenated essential oil remain unchanged for periods up to 120 h, while emulsions of D-limonene and *n*-hexadecane are unstable and their average diameter increases monotonically with time. The mechanism of emulsion destabilization with time in these systems was attributed to Ostwald ripening. Indeed, Ostwald ripening is the

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process whereby larger droplets grow at the expense of smaller ones because of the transport of dispersed phase molecules from the smaller to the larger droplets through the intervening continuous phase (Kabalnov & Shchukin, 1992). This phenomenon has very important consequences for instance in emulsified products that are to be stored for prolonged periods of time.

In the accompanying study, it was also observed that the mean droplet diameter of *n*-decane, *n*-dodecane, *n*-tetradecane and *n*-hexadecane emulsions immediately after preparation was in the range of 4–4.5 μm. While in orange oil emulsions, an average droplet diameter ranging from 2.5 to 3.0 μm was found (Acedo-Carrillo et al., accepted, 2006). The influence of the nature of the oil phase on the emulsifying behavior of gum arabic has also been investigated by Dickinson et al. (Dickinson, Galazka, & Anderson, 1991). In such studies, the time dependence of droplet-size distribution of oil-in-water emulsions made with *n*-hexadecane, D-limonene and orange oil found a different tendency of droplets coalescence between *n*-hexadecane on one hand and D-limonene and orange oil on the other, caused principally by the Ostwald ripening process (Dickinson, 1986). This, along with other instability mechanisms (e.g. gravitational separation, flocculation, coalescence) cause changes in the spatial distribution and/or size of the droplets, which may cause significant alterations in emulsion rheology (Weiss & McClements, 2000).

In addition, the rheological properties of emulsions are known to be affected by the contribution of attractive and repulsive interactions between the oil droplets, e.g. van der Waals, electrostatic, steric, depletion, and hydrophobic (Hiemenz & Rajagopalan, 1997; McClements, 1998; Tadros, 1996). When attractive interactions predominate the droplets tend to aggregate (e.g. flocculation and creaming), which increases their effective size and volume fraction due to the presence of a continuous phase trapped between the droplets in the flocs, thereby altering emulsion rheology (Tadros, 1996). While under the influence of repulsive forces, the effective volume fraction and size of the droplets is also increased, but this time because they are not able to approach as closely together as hard spheres (Buscall, Goodwin, Hawkins, & Ottewill, 1982). When the distance of closest approach is significant compared to the particle radius, these systems behave as though they have a particle concentration that is much greater than the actual droplet concentration. As a result they may be much more viscous than expected or even exhibit elastic behavior (Tadros, 1996). In a recent investigation, it has been observed that a sol–gel transition occurs when the mean droplet radius was decreased below a critical value of ~85 nm because of overlap of the electrical double layers surrounding the droplets (Weiss & McClements, 2000). Besides, when the surface-to-surface distance between droplets becomes less than twice the thickness of the electrical double layer (κ^{-1}) there is a strong electrostatic repulsion between the droplets that causes an emulsion to gain 'solid-like' characteristics (Buscall et al., 1982).

In the present study, it was therefore considered important to address the role of the nature of the oil phase on the bulk rheology of the emulsions stabilized mostly with mesquite gum. This emulsion by stabilizing polysaccharide has been studied less extensive than gum arabic. To this end, small-deformation rheology was utilized as the investigative tool. To our knowledge, this is the first experimental account of the ability of mesquite gum-stabilized orange oil-in-water emulsions which formed permanent viscoelastic gels upon standing, a behavior not found in similar emulsions stabilized with gum arabic. Many future potential applications of MG can be anticipated to rely on this property.

2. Experimental

2.1. Materials

Mesquite gum was collected manually 25 km west of the city of Hermosillo, Sonora, México. A hand-sorted batch comprising entire, amber-like clean nodules was ground in a hammer mill and used throughout the study without any further treatment. Gum arabic was an authenticated sample from *Acacia senegal* (Ex-Sudan) crude nodules, a kind gift from Prof. P. Williams of NEWI (Wales, UK). Unterpenated orange essential oil was obtained from a Mexican Company (Esencítricos S. de R.L., Tlalnepantla, México) and was used as received and kept in darkness at room temperature until used. D-limonene, *n*-decane, *n*-dodecane, *n*-tetradecane, *n*-hexadecane were all of analytical grade, from Sigma-Aldrich (México). The water used throughout was of 18.3 M Ω cm directly produced in a unit Easy Pure Instrument from Barnstead (Dubuque, Iowa).

2.2. Preparation of emulsions

MG solutions of 15% (w/w) were prepared by dissolving the crude gums in water by magnetic stirring at room temperature, filtered through Whatman No. 1 paper and stored for 24 h at 8 °C before use. Emulsions were prepared by mixing oil with MG solution using an Ultra Turrax T25 homogenizer (IKA Janke and Kunkel, Stafen, Germany) during 4 min at 5000 rev/min so as to yield a final oil fraction of 25% by volume. All emulsions were prepared immediately before being loaded into the rheometer.

2.3. Rheological determinations

The rheological properties of the emulsions were tested under small deformation using a strain-controlled Rheometrics RFS2 fluids spectrometer fitted with a stainless steel cone and plate tool (cone angle 0.04 rad, diameter 50 mm) and temperature control was exerted by a circulator bath and kept at 25 °C. At the end of each run, the dependence of the viscoelastic moduli on strain was determined. In a typical testing sequence, the emulsion was loaded to the rheometer immediately after being prepared and the following tests were conducted: (1) Dynamic time sweep ($\omega = 1.0$ rad/s; $\gamma = 0.05$; time $= 0$–2 h or until steady G' and G'' values were reached);

(2) Dynamic frequency sweep ($\omega = 0.1$–100 rad/s; $\gamma = 0.05$);
(3) Dynamic strain sweep ($\omega = 5.0$ rad/s; $\gamma = 0.1$–0.5).

3. Results and discussion

3.1. Influence of the oil phase on the small-deformation rheology of aged emulsions

The dependence of the mechanical properties of MG-stabilized oil-in water emulsions on the nature of the oil phase was studied using small-deformation oscillatory measurements. Disruption of any structuring bonds holding the droplets together are likely to be reduced using this type of measurements (i.e. as compared to steady shear tests). Mechanical spectra of MG-stabilized o/w emulsions with different oils are shown in Fig. 1 registered after aging times of approx. 1 h, at the end of the dynamic time sweeps (see below). In all cases the concentration of stabilizer (MG or GA) was 15% (w/w). For most of the alkanes used, the mechanical behavior was that of a viscoelastic liquid, where $G' < G''$ throughout the entire frequency range and in general the values of the shear modulus, G', remained at very low values (<1 Pa). Nonetheless, in the case of *n*-dodecane (Fig. 1a), we observed a weak-gel structure where $G'' < G'$ and both moduli increase with frequency under almost the same gradient (0.27 and 0.29, respectively); although both G' and G'' are relatively small (~ 0.2–1 Pa) and complex viscosity, η^*, decreases monotonically with a slope of -0.72. In the case of emulsions of D-limonene (Fig. 1b) and unterpenated orange essential oil (Fig. 1c) stabilized with GA, the emulsions remained as a liquid even after long storage periods (up to ~ 120 min), as evidenced by the mechanical spectrum shown in Fig. 1b, where G'' values exceed those of G' over the whole frequency range. In contrast, the mechanical spectrum of MG-stabilized emulsions containing orange oil (Fig. 1d) showed the characteristic behavior of a gel-like network, namely predominance of G' over G'' and little dependence of G' on frequency. Both viscoelastic moduli in such system show quadratic increase with frequency and the power of the complex viscosity, η^*, with frequency decreases with a slope of -0.88 (Dickinson & Pawlowski, 1995). All these features are unequivocal evidence that a gel network is being set up in *n*-dodecane and orange essential oil MG-stabilized emulsions. In turn, the corresponding mechanical spectra of emulsions of D-limonene stabilized with MG (not shown), show much lower values of the viscoelastic moduli as compared with orange oil emulsions, although an incipient gel network behavior seems evident in these emulsions too, G' and G'' vary with frequency with almost identical power (0.35 and 0.39, respectively). For both D-limonene and orange oil MG-stabilized emulsions, the overall values of G' and G'' are about an order of magnitude larger than those of the emulsions formed with the alkanes.

Fig. 2 shows the strain dependence of G' and G'' for the emulsion of orange oil stabilized with MG (corresponding to Fig. 1c). It is interesting to point out that at the strain used to perform the rheological determinations of this work, $\sim 20\%$, the system was within the linear viscoelastic region. It is also

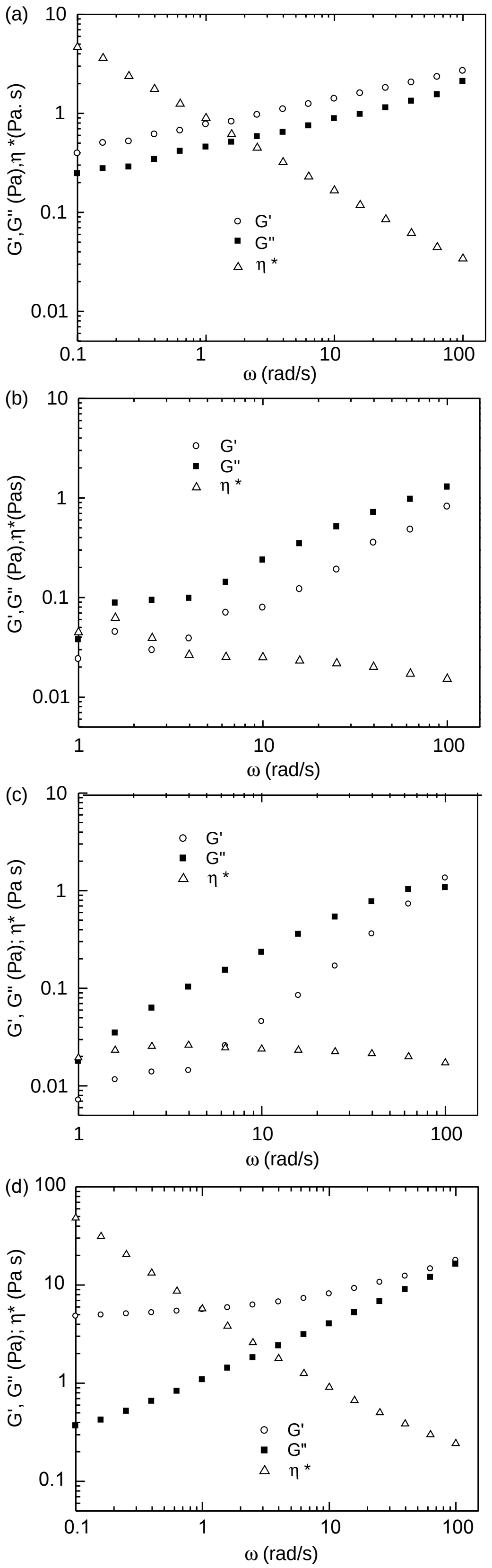

Fig. 1. Frequency dependence of the shear storage, G', and loss, G'', moduli and of the complex viscosity, η^*, after aging of oil-in-water emulsions (25% (v/v) oil, 25 °C, $\gamma = 0.05$) as: (a) 15% (w/w) mesquite gum and *n*-dodecane; (b) 15% gum arabic and D-limonene; (c) 15% (w/w) gum arabic and orange essential oil and (d) 15% (w/w) mesquite gum and orange essential oil.

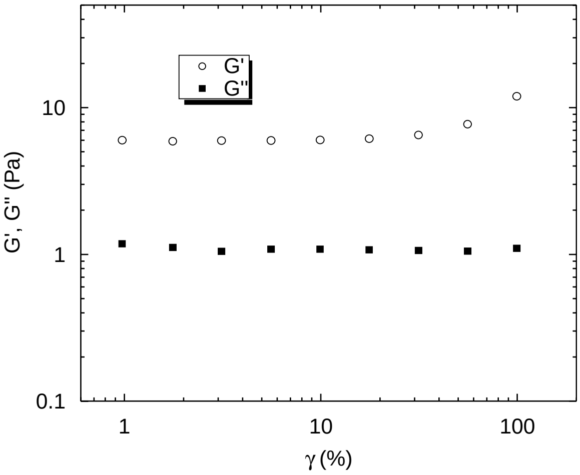

Fig. 2. Strain dependence of the storage, G', and loss, G'', moduli of an emulsion of orange essential oil (25% (v/v) oil, 25 °C, $\omega = 5$ rad/s) stabilized with 15% (w/w) mesquite gum.

interesting to notice that as the strain grows, G' increase. This shear hardening effect observed in MG emulsions can be envisaged as arising from a closer packing of microgelled colloidal particles leading to greater friction forces between the droplets subjected to shear. Similar behavior has been observed in gellan gels at high ionic strength (Tsiami, Morris, & Brownsey, 1994). This experiment also confirmed that the frequency sweep measurements were performed within the linear viscoelastic region.

The dramatic observed differences in mechanical properties of the emulsions addressed in this study were associated to both the type of oil and that of gum, thus effectively, reflecting that highly specific mechanisms seem to underlie the behavior of these systems. Although hydrophobic interactions between the oils and the proteins in MG or gum arabic at the interface may account for the relaxation and overall mechanical properties, they cannot be claimed as being the only responsible mechanism controlling the strength of the aggregation of the emulsion droplets, hence the rheological properties of the emulsions. The influence of other components comprised in orange oil and that may interact directly with either protein or polysaccharide components of MG in the continuous phase, could also affect the gel formation in the emulsions. Indeed, Dickinson & Pawlowsky (1995) have demonstrated the influence of polysaccharide–protein interactions on the rheology of o/w emulsions stabilized by different proteins and found thickening effects and development of gel like structures in the emulsions.

3.2. Response of the emulsions with time

As shown above, the case of MG-stabilized emulsions with alkanes, weak-gel behavior was demonstrated from *n*-dodecane, however, it was of interest to understand the relation between the length of the alkane chain and the kinetics of the gelling process. Hence, further insight to the behavior of these systems was gleaned from the time course evolution of the elastic, G', and the loss, G'', moduli. The criterion adopted so as to mark the critical gel point, t_{gel}, was the crossover of G' and G''. The dependence of this parameter with frequency was also studied. The t_{gel} marks the point of the incipient creation of a permanent gel network as a function of the control variable, in this case time.

Table 1
Shear storage modulus, G', and t_{gel} for oil-in water emulsions of various types of oils stabilized with mesquite gum and gum arabic (15%, w/w)

Oil	t_{gel} (s)	G' (Pa)
n-hexadecane/MG	8243	0.56
n-tetradecane/MG	0[a]	0.56
n-dodecane/MG	830	0.6
n-decane/MG	4221	1.5
Orange oil/MG	2198	6.93
D-limonene/MG	463	1.17
D-limonene/AG	No gel[b]	1.24

[a] 0 means that both G' and G'' curves are almost the same.

[b] No gel means that G'' is always larger than G' during the time of the experiment.

Our results show that for the case of the alkanes used, the t_{gel} is shorter for the oil of larger chain length. In Table 1 are shown the t_{gel} data for the different oils used. The value 0 means that both G' and G'' have approximately the same value during the test and no gel means that the value of G'' is larger than the one of G' throughout the time scale. We noticed that the gel formed with these oils is less weak for *n*-dodecane and *n*-decane at the higher frequency used, showing relative larger G' values.

In the case of MG-stabilized emulsions with D-limonene and orange oil, we observed that the gel strength (i.e. G' values) was larger than the rest of the studied emulsions. Also, D-limonene produces only a very weak gel with very similar mechanical properties between MG- and GA-stabilized emulsions.

In Fig. 3 is illustrated the time course evolution of G'' and G' for an emulsion of orange oil with mesquite gum. Initially, the loss modulus, G'', increases with time, while the storage modulus, G', keeps below the noise level. After a certain time, G' suddenly begins to increase rapidly and eventually exceeds G''. At longer times, both G' and G'', and hence tan δ, attain

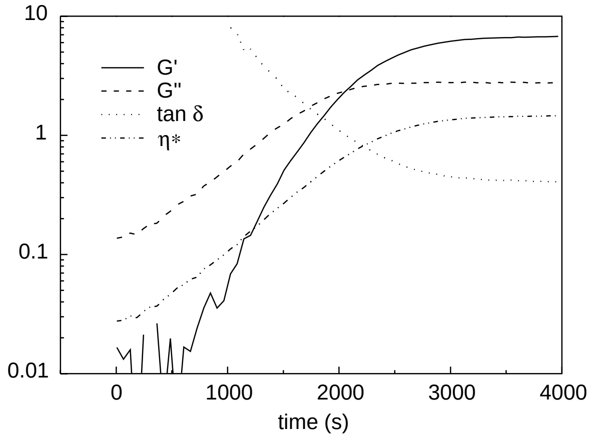

Fig. 3. Time evolution of the storage modulus, G', loss modulus, G'', tan(δ) and complex viscosity, η^*, for an orange essential oil emulsion stabilized with 15% (w/w) mesquite gum at 25 °C ($\omega = 2.5$ rad/s; $\gamma = 0.05$).

steady values. The crossover point between G' and G'' was adopted here as the criterion to mark the critical rheological gel time, t_{gel}, or the onset of incipient formation of the gel network or the percolation threshold (i.e. the instant when the system is assumed to have formed the first cluster of infinite molar mass) (Tung & Dynes, 1982). Critical gel times, t_{gel}, calculated under this condition are known to be dependent on frequency as demonstrated in the rigorous theoretical argument by Winter & Chambon (1986). However, in many instances the application of the Winter–Chambon criterion is either not experimentally feasible, nor rheological measurements at the critical gel point can be guaranteed to be at the linear viscoelastic region. The behavior of $\tan\delta$ with time is also characteristic of a viscoelastic liquid at short times (around 90°) and reaches a value characteristic of an elastic solid (near 0°) at larger times. In the literature some authors have considered the gel point as the time where the elasticity (G') first appears (t_c) and this issue has been addressed using percolation theories. We have analyzed the data recorded for emulsions where gel formation was found using several approaches, and have compared our results with the near linear model proposed by Pope & Mackenzie (1988) and by Van Cantford, Brasseur, Michaux, Pirad, & Pirad (1995), a model derived from percolation theory (Gauthier-Manuel, Guyon, Roux, Gits, & Lefaucheux, 1987).

In the nonlinear model of Pope and Mackenzie, they arrive to a linear relationship between the complex viscosity, η^*, and the time t/t_g

$$\ln(\eta^*) = B + m\ln[\alpha/(1-\alpha)] \tag{1}$$

where $\alpha = t/t_{\mathrm{gel}}$, B is a constant and m is a constant which depends on the nature of the system. Van Cantfort, Brasseur, Michaux, Pirard, and Pope & Mackenzie (1988) have found a linear behavior by using this model and emulsions of $BaTiO_3$ in the range of $t/t_{\mathrm{gel}} = 0.75$ and 0.90, where the sol–gel transition was observed. This sol–gel transition they found was associated to the aggregation of spherical particles to form an average linear network.

The percolation approach is used to understand the properties of emulsions near the percolation threshold. It is expected first that the viscosity of the sol diverges as the cluster size increases as it approaches the threshold

$$G'' = k'[(p-p_c)/p_c]^{-k} \tag{2}$$

where the control parameter p (at the threshold) is proportional to the number of effective bonds and p_c is the critical value where an infinite cluster first exists, k' is a scaling factor.

After that, the elasticity of the gel, starting from zero, increases continuously above the threshold due to the formation and consolidation of the infinite cluster. Near the threshold

$$G' = k''[(p-p_c)/p_c]^{\mu} \tag{3}$$

where k'' and μ are expected to be independent of the material.

Van Cantfort et al. (1995) and others differentiate two different mechanisms to explain the sol–gel transition. In the first mechanism, the rigid objects composing the network (particles, agglomerates or strong chains) are free to rotate around of some of their links, different conformations are possible and the entropy is associated with the system, so that the elasticity is the result of changes of conformation. In the

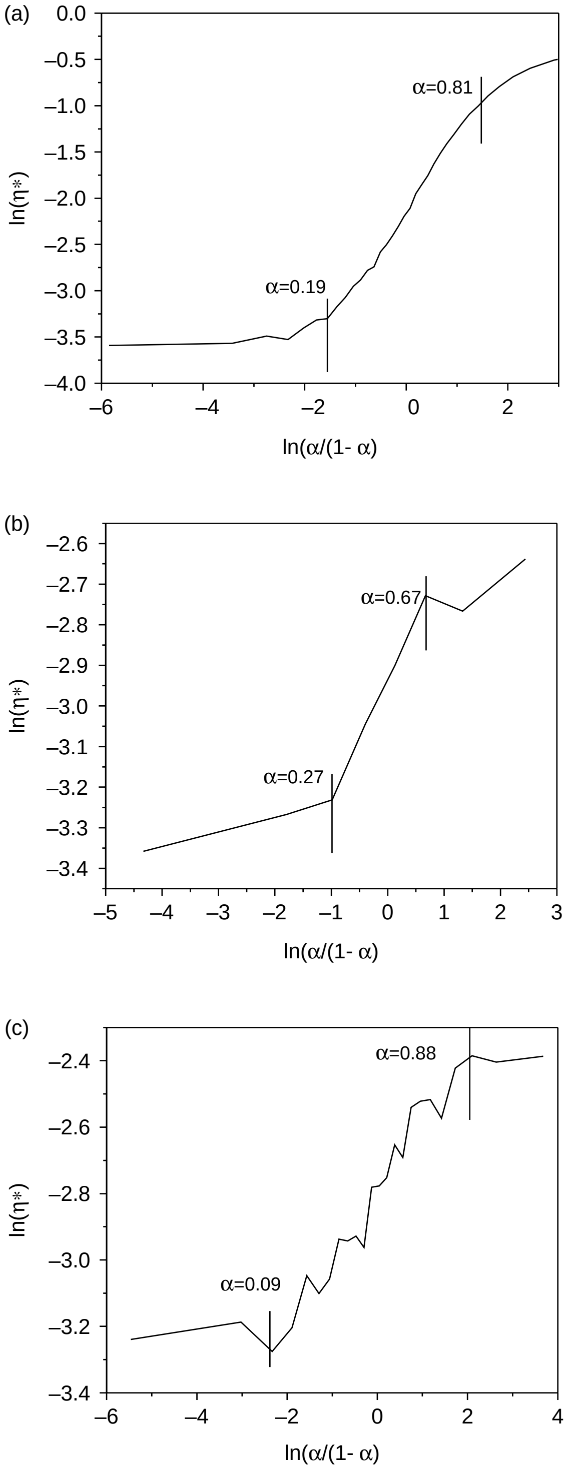

Fig. 4. The variation of $\ln(\eta^*)$ vs $\ln[\alpha/(1-\alpha)]$, α as defined in the text, for the case of a 15% (w/w) mesquite gum and gum arabic emulsions prepared with different oils at the frequency $\omega = 5$ rad/s. The vertical lines are drawn only to visualize the three regions. (a) Mesquite gum and orange oil, (b) mesquite gum and D-limonene, (c) gum arabic and D-limonene.

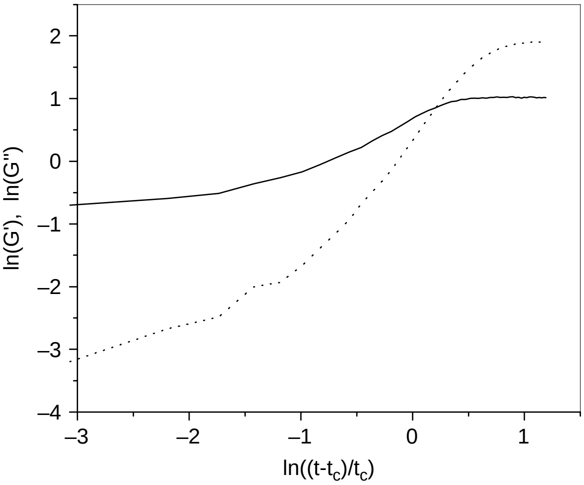

Fig. 5. Behavior of $\ln(G')$ and $\ln(G'')$ vs $\ln(t-t_c)/t_c)$ for the emulsion of orange oil-in-water stabilized with 15% (w/w) MG. (dotted line, $\ln(G')$), (solid line, $\ln(G'')$).

second mechanism, the objects are totally rigid and the forces are transmitted through bending of the weakest links. They calculated the critical exponent μ and obtained a value near 2. For the other mechanism, they obtained a value between 3.5 and 4.4.

We applied these two models to analyze the gelling behavior of MG-stabilized o/w emulsions at the three studied frequencies. In Fig. 4a is shown the variation of $\ln(\eta^*)$ vs $\ln[\alpha/(1-\alpha)]$ (Eq. (1)) for the case of orange oil at $\omega=5$ rad/s. We observe a fairly linear behavior between $\alpha=0.19$ and 0.81. This interval of time corresponds to the time before G' and G'' cross each other, but when the elastic modulus starts to grow. Notice that the value $\ln[\alpha/(1-\alpha)]=0$ corresponds to a time $t=t_{\mathrm{gel}}/2\approx 1000$ s, which is very near to the experimental $t_{\mathrm{gel}}/2$ value ($\sim$923 s). The behavior of $\ln(\eta^*)$ for the other frequencies is similar. We found three linear regions. One at the beginning, where the viscoelastic behavior is dominant, the next one is around $t=t_{\mathrm{gel}}/2$, where the transition to a more aggregated system and the formation of a linear network is observed, according to Van Cantfort et al. (1995), and the last one when G' is larger than G''. In the case of MG-stabilized emulsions with D-limonene, we found the same three linear regions for $\ln(\eta^*)$, but the intervals dividing these regions were different (Fig. 4b) than those of the orange oil emulsions. In the case of the alkanes studied, we could only obtain these three linear regions for hexadecane and tetradecane emulsions and only for one frequency. One of the surprising result is that GA with D-limonene only showed the linear behavior of $\ln(\eta^*)$ when the oscillation was at 10 rad/s, but the transient region (central region) showed high fluctuations perhaps indicative of the weak interactions established between the emulsion droplets while building a tenuous network (Fig. 4c).

The results for the behavior of $\ln(G')$ vs $\ln((t-t_c)/t_c)$ from Eq. (3) is shown in Fig. 5 for the emulsion of orange oil-in-water stabilized with MG. We obtained a linear behavior around $\ln((t-t_c)/t_c)=0$, where $t=t_c/2$. In this interval we found a slope of 2.2 and for $\omega=10$ and 5 rad/s we obtained 2.1 and 1.5, respectively. These values are very similar to the one found by Van Cantfort et al. (1995) (ca. 2) by studying the sol–gel transition of $BATiO_3$ emulsions. This behavior is explained with a scalar elasticity model and confirmed by Gauthier-Manuel et al. (1987) in a different interval of time.

We measured the parameter μ for the case of D-limonene and MG and found a value around 1 or less. For the alkanes analyzed, we obtained a slope less than 1. This could mean that the network formed is really very weak and the scalar elasticity model is not appropriated to explain the phenomenon.

4. Conclusions

In this work we have performed rheological measurements of mesquite gum-stabilized oil-in-water emulsions. Orange oil-in-water emulsions stabilized with mesquite gum showed unequivocally the ability of gel formation. By contrast, gum arabic-stabilized emulsions showed only fluid behavior with all oils used in this work. As a first approach, we venture to suggest that the weak gelling phenomenon shown on MG-stabilized emulsions with orange oil in the dispersed phase arises from an electrosteric interaction between the charged oil spheres dispersed in a continuous aqueous phase where a weak gel network is set up involving protein and polysaccharide molecules of MG attached to the oil spheres themselves similar to networks found in other gelling processes explained with models derived from percolation theories. The nature of the crosslinks (chemical or physical) in this putative gel network and the role of the variation of the phase volume salt concentration and temperature are being the subject of current ongoing studies in our laboratories.

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