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ORIGINAL CONTRIBUTION

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Investigation of the interactions in emulsions stabilized by a polymeric surfactant and its mixtures with an anionic surfactant

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Abstract The interaction of a nonionic polymeric surfactant with an anionic surfactant at the oil–water interface has been studied by its effects on the droplet size, stability and rheology of emulsions. Oil-in-water (o/w) emulsions were prepared using isoparaffinic oil and mixtures of a nonionic polymeric surfactant with an anionic surfactant. The macromolecular surfactant was a graft copolymer with a backbone of polymethyl methacrylate and grafted polyethylene oxide (a graft copolymer with PEO chains of MW = 750). The anionic surfactant was sodium dodecyl sulfate (SDS). The stabilization of the emulsion droplets was found to be different when using one or the other surfactant. The mechanism of stabilization of emulsion droplets by the macromolecular surfactant is of the steric type while the stabilization by anionic surfactant is of the electrostatic repulsion type. Emulsions stabilized with mixtures present both types of stabilization. Other effects on the preparation and stabilization of emulsions were found to be dependent on properties associated with the surfactant molecular weight such as the Marangoni effect and Gibbs elasticity. The initial droplet size of the emulsions showed a synergistic effect of the surfactant combination, showing a minimum for the mixtures compared to the pure components. Emulsion stability also shows a synergistic interaction of both surfactants. Rheological measurements allow for the estimation of the interparticle interaction when measured as a function of volume fraction. Most of the effects observed can be attributed to the differences in interfacial tension and droplet radius produced by both surfactants and their mixtures. The elastic moduli are well explained on the basis of droplet deformation. Ionic versus steric stabilization produce little difference in the observed rheology, the only important differences observed concerned the extent of the linear viscoelasticity region.

Key words Emulsion – rheology – polymer – surfactant interaction

Introduction

The interaction between surfactants and polymers has been the subject of numerous investigations [1]. Most of the studies were carried out at the air/liquid interface and have illustrated the nature of the interaction between surfactant ions and their micelles with several nonionic polymers. However, few investigations have been carried out at the oil/water interface [2] in spite of their importance in emulsion formation and stability.

In this paper, we present results concerning the interaction of a polymeric surfactant (a graft copolymer of polymethyl methacrylate and polyethylene oxide) with an anionic surfactant (namely, sodium dodecyl sulfate, SDS) at an oil–water interface. For this purpose, emulsions stabilized only by the polymeric surfactant or by the ionic surfactant have been compared with emulsions stabilized by their mixtures. Two aspects have been studied:- the emulsion stability and the rheology of the emulsions. Emulsions formed using the polymeric surfactant are sterically stabilized whilst emulsions prepared using the anionic surfactant are electrostatically stabilised. Mixtures are expected to show both types of stabilization and therefore should have higher stability, in particular, against flocculation and coalescence. In addition, other dynamic effects due to the widely different molecular size of the surfactants are expected. This difference will have effects on the diffusion rates, adsorption and Gibbs elasticity.

The adsorption of the polymeric surfactant is expected to be a relatively slow process, much slower than the adsorption of SDS due to differences in their diffusion coefficients. Important differences with respect to the Marangoni effect and the Gibbs elasticity are also expected [3–5]. The Gibbs elasticity shows a maximum as a function of surfactant concentration. At low concentration, the elasticity increases due to the increase in adsorbed matter and at high concentration there is a reduction due to faster diffusion. The Gibbs elasticity is expected to be higher for the higher molecular weight surfactant due to its lower diffusion coefficient. In addition, the formation of SDS micelles provides a reservoir of monomers that reduces the relaxation time to reach the equilibrium concentration after disturbing the interface. The dynamic interfacial tension and the Gibbs elasticity of the surfactant mixtures were investigated by Garret and Joos [6]; they found that the Gibbs elasticity as a function of measured frequency showed two plateaus instead of the single one found for single surfactants. These plateaus correspond to the limiting frequency at which each surfactant behaves as an insoluble monolayer. The equilibrium adsorption behavior of surfactant–polymer mixtures is reasonably well understood [6, 7]. However, there is a lack of information on the interaction of emulsion droplets stabilized in this way. Addition of an ionic surfactant to a water-soluble polymer has been studied by several authors [8]. They found that addition of a water-soluble polymer to SDS solutions resulted in two apparent critical-micellization concentrations. The first transition, that is independent of polymer concentration, marks the beginning of association of the surfactant with the polymer. The second, dependent on polymer concentration, marks the saturation of the polymer binding sites and the beginning of normal surfactant micellization. Equilibrium surface tension is dependent only on the surfactant characteristics provided its concentration is above the second CMC. They found for SDS and polyoxyethylene that these values were independent of polymer chain length provided the polymer was sufficiently high in molecular weight. For short chains, with a molecular weight less than 1000 there was some dependence on molecular weight. This was probably due to formation of mixed micelles.

The rheology of the emulsions is expected to provide information on the interparticle interaction [9–11] as well as on the deformation of the interfaces [11]. Differences on the interparticle interactions are due to the differences in the nature of the stabilizing molecules while differences in particle deformation are due to the different adsorption behavior. One would expect a large difference between emulsions stabilized by SDS (soft interaction) when compared to systems stabilized by the graft copolymer (which is closer to hard-sphere interaction). It was of interest to investigate the effect of SDS addition on the rheology of emulsions that were stabilized using the graft copolymer.

Materials and methods

The polymeric surfactant Atlox 4913 was obtained from ICI surfactants (Everberg, Belgium) and used as received. Atlox 4913 is a polymeric surfactant of the graft type. A backbone of polymethyl methacrylate is grafted with polyoxyethylene oxide of M = 750. The polymer is supplied as a solution consisting of ~33% polymer, ~33% water and ~33% propylene glycol. SDS was purchased from BDH (Biochemical Specially Pure) and used as received. The oil Phase was *Isopar M* (supplied by Exxon, UK), an isoparaffinic oil with boiling point in the range 207–254 °C. The *water* was doubly distilled in an all Pyrex glass apparatus.

Emulsion preparation

Aqueous solutions of the surfactants and their mixtures were used as the continuous phase. To these solutions the required amount of oil was added while mixing at a low shear rate. Once the required amount of oil was added (70% w/w) the emulsion was sheared for increasing lengths of time at 20 000 r.p.m. The droplet size was measured after different times and the process was stopped when the mean size and droplet size distribution did not change with further shearing.

The *droplet size* of the emulsion was determined using a Coulter Multisizer II (Coulter Electronics) after dilution in Isoton II. The possible aggregation of the emulsion droplets was checked by comparing the results obtained with that of samples previously diluted in a 1% Brij35 solution. No difference was observed between samples with or without adsorption of this nonionic surfactant.

The *interfacial tension* was measured using a Wilhemy Plate attached to a Robal microbalance (CI Electrobalance) with a sensitivity of 10 μg. The aqueous and the oil phases were separated from the emulsion by high-speed centrifugation and these were used as the lower and higher phases, respectively. The upper phase was carefully added on top of the lower phase after the Wilhemy Plate was already inserted in the lower phase. The weight was followed as a function of time until no significant changes were observed for two hours. The reproducibility of the measurements was better than 0.1 mN m^{-1}.

Viscoelastic measurements were performed using a Bohlin VOR rheometer (Bohlin Rheologie, Lund, Sweden) fitted with a concentric cylinder measuring system C14. The samples were placed in the cup and the bob was carefully lowered into the sample. Moderate shear applied to selected samples did not change its viscoelastic parameters and the experiments were made 5 min after inserting the bob. Care was taken to avoid drying of the samples; therefore a thin layer of paraffin oil was carefully placed on the top of the sample. This oil layer did not mix with the emulsion and prevented any measurable drying for hours. The rheometer is a controlled strain instrument that permits oscillatory measurements. Firstly, the elastic (G') and viscous (G'') moduli were measured as a function of strain at a given frequency (typically 0.1 Hz). This allows one to obtain the linear viscoelastic region in which the rheological parameters are independent of the applied strain. Once this parameter was determined, a frequency sweep was carried out at a strain that corresponds to the linear region. The frequency span used corresponded to the region between 10^{-3} and 10 Hz.

Results

The initial droplet size depended on the composition of the system. Upon addition of SDS to the polymeric surfactant, the droplet size decreased from the value obtained in absence of SDS. The droplet size was also lower than that produced using SDS alone; these results are summarized in Table 1 which also shows the interfacial tension values. This clearly shows the synergistic effect obtained with the polymer–surfactant systems when compared with the results obtained with the pure components.

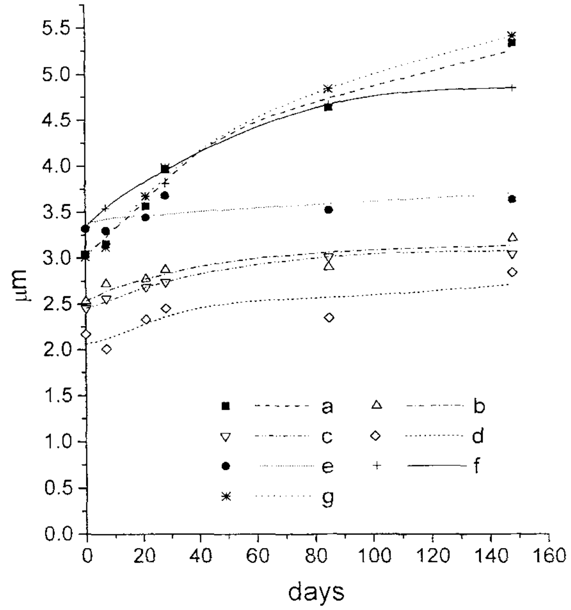

Fig. 1 Emulsion droplet diameter (D_{32}) as a function of time. The codes for emulsion composition are given in Table 1

Table 1 Composition of the emulsions tested, weight fraction of SDS and Atlox 4913 based on the total emulsion weight (all emulsions are 70% oil weight fraction), emulsion droplet diameter (D_{32}) and equilibrium interfacial tension between the aqueous and hydrocarbon phases

Emulsion code	SDS	Atlox 4913	D_{32}/μm	γ/mN m^{-1}
a	0.00	0.04	3.04	9.07
b	0.01	0.03	2.53	6.08
c	0.02	0.02	2.45	5.25
d	0.03	0.01	2.17	5.00
e	0.04	0.00	3.32	5.25
f	0.00	0.05	3.34	8.85
g	0.00	0.03	3.01	9.07

Emulsion droplet size was measured as a function of time for emulsions stored at 40 °C. These results are shown in Fig. 1 (the codes of their composition are given in Table 1). The evolution of emulsion droplet size with time (Fig. 1) shows two types of behavior. Emulsions prepared with the polymeric surfactant alone show a continuous increase of droplet size with time. Emulsions prepared with SDS alone or mixtures of this with the polymeric surfactant show a lower rate of coalescence when compared with the polymeric surfactant alone.

The interfacial tension results (Table 1) show that systems c and d have interfacial tensions that correspond to that of the system with SDS alone (system e) and therefore, the adsorption at the interface is dominated by the presence of SDS in the system. The interfacial tension for the

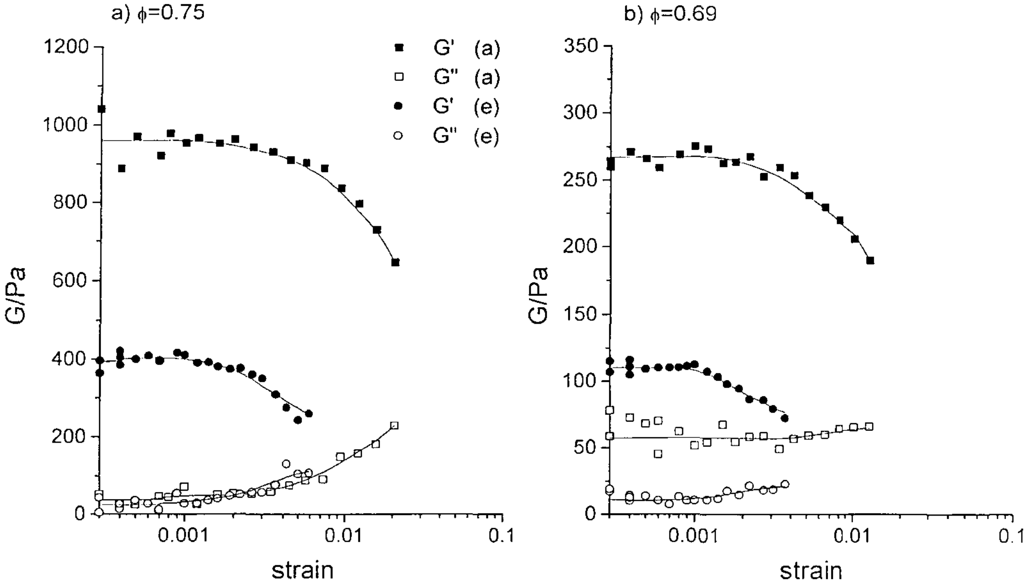

Fig. 2 G' and G'' as a function of strain at 0.1 Hz for emulsion a and e. (a) volume fraction $\phi = 0.75$; (b) $\phi = 0.69$

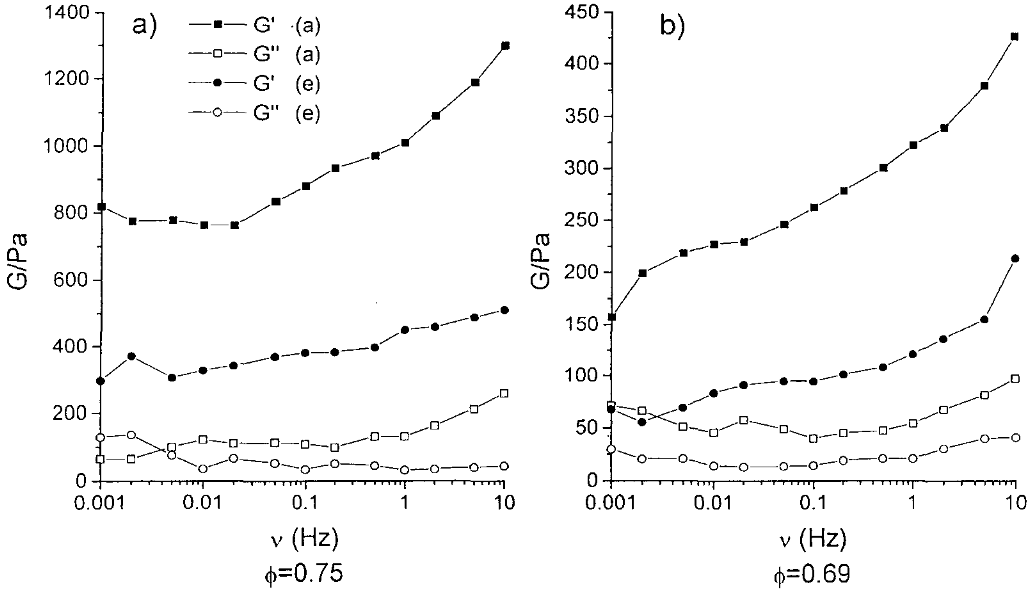

Fig. 3 G' and G'' as a function of frequency in the linear viscoelastic region for the same samples as in Fig. 2

polymeric surfactant alone is almost double that in the corresponding system with SDS. The dependence of the interfacial tension on the concentration of polymeric surfactant is very small at the concentrations used (compare systems a, f and g in Table 1). This independence of the interfacial tension on the concentration suggests that the interface is saturated at these concentrations. An intermediate interfacial tension is obtained for composition b, this could to be due either to adsorption of SDS on the polymer [8] or displacement of the polymer by SDS molecules. It should be noted that even for this system the concentration of SDS is well above its CMC which is 0.00813 mol dm^{-3} [12], i.e., 14 times higher. In addition the concentration of the polymeric surfactant is very high as well.

From the evolution of the interfacial tension with time of newly formed interfaces it was observed that an equilibrium value was reached more slowly for the polymeric surfactant. In the mixtures of both surfactants the interfacial tension rapidly decreased to a value close to that of

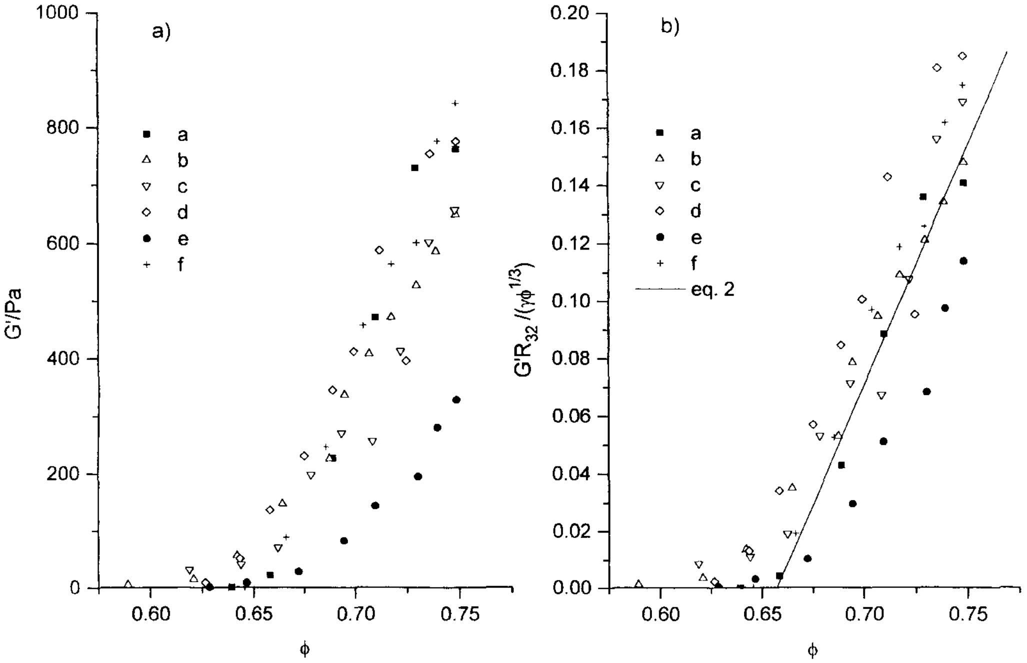

Fig. 4 (a) G' at 0.1 Hz as a function of volume fraction for emulsions of compositions given in Table 1. (b) $G'R_{32}/\gamma\phi^{-1/3}$ at 0.1 Hz as a function of volume fraction for the same emulsions as (a)

equilibrium, the same behavior was observed with SDS. However, the composition of the mixture at the interface is probably changing with time from almost pure SDS to the equilibrium mixture.

Figure 2 shows the variation of G' and G'' with strain for the emulsion formed with the polymeric surfactant alone (a) and the anionic surfactant alone (e), at two different volume fractions (0.75 and 0.69, respectively). G' shows a plateau at low strain for all the systems studied with a reduction above a critical strain value. The behavior of G'' is the opposite, a plateau at low strain with an increase at high strain. The critical strain, at which the rheological parameters start showing dependence with strain, depends on the system. A reduction in volume fraction or the change from emulsion a to emulsion e decreases the values of this critical strain.

Figure 3 shows the variation of G' and G'' with frequency ν (Hz) at a fixed strain in the linear viscoelastic region for the same emulsions as Fig. 2. There is a dependence of the moduli with frequency. This dependence is higher for the emulsions stabilized with the polymeric surfactant than for those stabilized by SDS. The dependence with frequency is also dependent on the volume fraction. The lower volume fraction emulsions show a larger dependence on frequency as would be expected.

In Fig. 4a, G' is represented as a function of dispersed phase volume fraction for the emulsions a to f at a frequency of 0.1 Hz in the linear viscoelastic region. Above a threshold volume fraction G' increases linearly with volume fraction. The results for the emulsion stabilized by SDS alone (e) are clearly below the results of the other emulsions.

Discussion

The reason why the polymeric surfactant alone does not effectively prevent coalescence is not clear. The droplet size of the emulsions tested is rather big to attribute any measurable effect to the different Ostwald ripening rates resulting from the different interfacial tensions [13]. Size effects do not seem to produce significant effects either; although the emulsions prepared using polymeric surfactant alone have bigger droplet size than the mixtures, the droplet size of the emulsion prepared using SDS alone is of the same order of magnitude. It is likely that the polymeric surfactant with its "rigid" backbone cannot fully cover the interface, thus, producing some "bare" patches which can induce coalescence. Interfacial tension and interfacial elasticity seem to be the only parameters in which these emulsions differ significantly. This differential rate of adsorption could create an enhanced Marangoni effect for the systems containing polymeric surfactant. This could explain the observed synergistic effect on the formation of small droplets for the mixtures of surfactants. An enhanced Marangoni effect could prevent coalescence during emulsification [3–5]. One can envisage that the fast diffusing SDS molecules will transfer liquid to the interfacial region thus preventing any thinning of the liquid film between the droplets. They will have an overall effect of reducing coalescence during emulsification.

Concerning the rheological results, the linear dependence of G' on volume fraction can be interpreted on the basis of droplet deformation. As the emulsion droplets pack together straining of the system implies the deformation of the droplets and this produces a macroscopic elastic modulus. According to Princen [14] the elastic shear modulus of an emulsion above the volume fraction of close packing takes the form

$$G_0 = a\frac{\gamma}{R_{32}}\phi^{1/3}(\phi - b), \tag{1}$$

where γ is the interfacial tension, R_{32} is the volume-surface mean radius, ϕ is the volume fraction and the parameters take the values $a = 1.76$ and $b = 0.712$. This equation is based on a model of cylinders packed in a hexagonal array and adapted to three-dimensional systems with the values of the parameters obtained from experiments on highly concentrated oil-in-water emulsions [14]. The shear modulus can be substituted by the dynamic elastic modulus provided it does not depend on the frequency [15]. As we have seen, the elastic modulus for the emulsions tested here presents some dependence on frequency and therefore, Princen's equation cannot be properly applied. However, its use can provide a means of evaluating the importance of the droplet deformation. Princen's equation can be linearized as

$$G_0\frac{R_{32}}{\gamma}\phi^{-1/3} = a(\phi - b) \tag{2}$$

to calculate the values of the parameters a and b. This is shown in Fig. 4b where the same data as in Fig. 4a are linearized using the form shown in Eq. (2). The scaling given by Princen's equation moves the curves closer together. This suggests that most of the effects on the elasticity are accounted for by the deformation of the emulsion droplets. The differences in slope and in the value of constant b in Eq. (2) may be explained in terms of the different surfactants used.

The value of b is probably related to the volume fraction of close packing of spheres [11, 13]. This value is normally considered to be about 0.68 that is the close packing value for a cubic arrangement of spheres [11]. Polydispersity could increase this value. Some reduction of the volume fraction of maximum packing can be observed for small particles if there is an adsorbed layer [9, 11, 16]. The difference with the value obtained by Princen could be due to the combination of lower polydispersity and a lower droplet diameter. The differences in slope could be due to the different surfactant used although the variation is not clear.

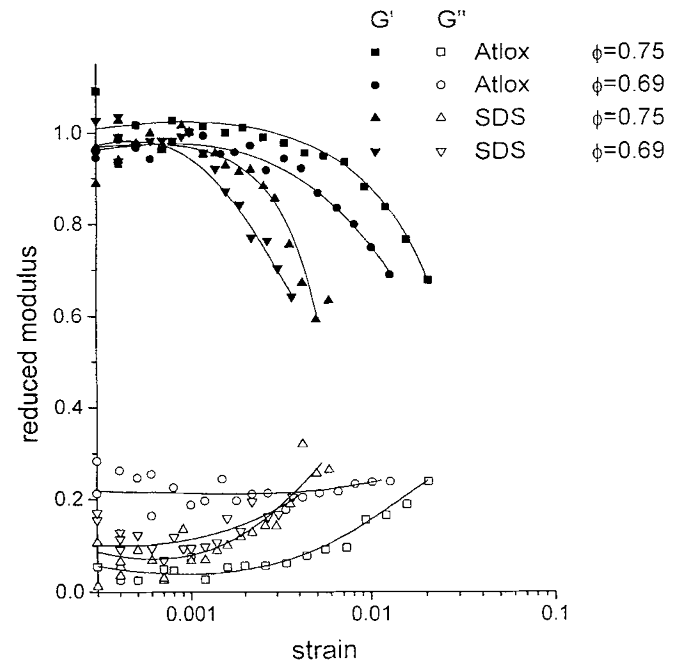

Fig. 5 G' and G'' normalized to the value of G' at a strain of 10^{-3} for the same samples as Fig. 2

The data of Fig. 2 can be normalized by dividing each series by the value of G' at a strain within the linear region (for instance a strain of 10^{-3}). This normalization eliminates most of the effect of different droplet size, interfacial tension and volume fraction. This is shown in Fig. 5. The emulsions with volume fraction 0.75 start the decrease of G' at higher strain than those of volume fraction 0.69. There is a clear dependence on the surfactant used as well. The emulsions stabilized with the polymeric surfactant have longer linear regions than the emulsions stabilized with SDS.

The appearance of nonlinearity can be due to several causes but, in general, it implies a rearrangement of the system to reduce the energy. In emulsions above the threshold of close packing (highly concentrated emulsions) several causes of nonlinearity have been pointed out [11, 17, 18]. On the one hand, the model proposed by Princen produces a constant modulus provided the strain remains below 0.3 or higher depending on the volume fraction [17]. This value is much higher than that observed for real systems, and therefore, this is probably not the reason for the observed behavior. The polydispersity and disorder of the system can cause nonlinear behavior as well [18]. However, the deviation from linearity could remain small for small strains according to simulations of the rheological behavior of bidimensional froths [18].

A third phenomenon that could induce nonlinearity is the fact that the strain of the system in addition to deformation of the droplets produces changes in the interparticle distance and therefore in the interaction potential. Indeed, some indication of this was found in the variation of critical strain of emulsions–suspension mixtures [11]. Pons et al. [11] have shown that the linear region of mixtures of solid particles and emulsions depends on the centre-to-centre distance for volume fractions below the volume fraction at which the systems start to show more elastic than viscous response. Above this limit the extent of the linear region increased for emulsions in an exponential way with volume fraction. This seems to indicate that at low volume fraction the observed nonlinearity is due to the change that the applied deformation causes in the interparticle distance while at higher volume fractions this contribution decreases and the nonlinearity could be caused by other causes such as the polydispersity and disorder of the emulsion. The closer the particles pack, the higher the strain to change the configuration to a new configuration of lower energy.

The difference in the type of interaction potential could account for the difference in behavior between the polymeric surfactant and the anionic surfactant. The interparticle potential for the SDS emulsion is of the compressed electrical double-layer repulsion type (the concentration of SDS is high) while for the polymeric surfactant the interaction is that of steric repulsion. Therefore, a change in the interparticle distance would have a different effect on the ionic stabilized emulsion than on the sterically stabilized.

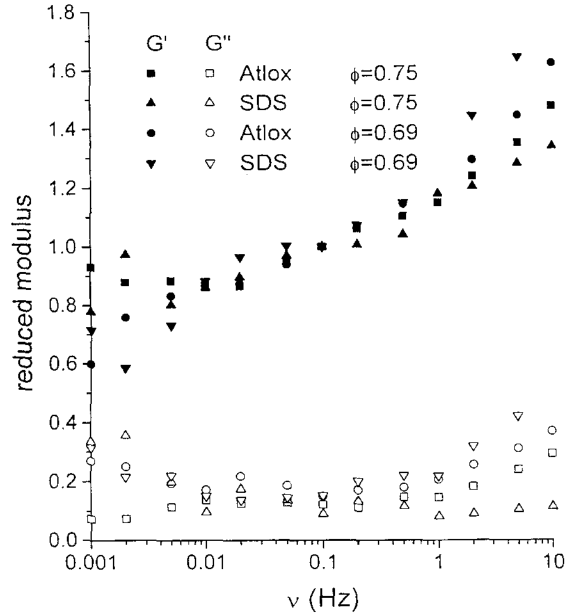

Fig. 6 G' and G'' normalized to the value of G' as a function of frequency for the same samples as Fig. 3

The dependence of the elastic modulus with frequency could be due to two effects. If the bending of the interfaces is not an instantaneous phenomenon, increasing the frequency will change the relative contributions of the two phenomena responsible for the elasticity; the bending of the interfaces and the interparticle interaction in the resulting modulus. At low frequency the interfaces could deform maintaining the interparticle interaction approximately constant; however, at high frequency the droplets would behave closer to undeformable spheres and the change in the interparticle distance would be the major effect. The second contribution to the frequency dependence could be the increasing importance of the Gibbs elasticity. The higher molecular weight of the polymeric surfactant would mean a lower diffusion rate of the surfactant, and therefore, the dynamic interfacial tension would be higher than the equilibrium value [4]. This effect would be stronger for the polymeric surfactant than for the low molecular weight surfactant. Normalization of the data of the series shown in Fig. 3 by the value of G' at 0.1 Hz (Fig. 6), shows that the dependence of G' with frequency is not very different for the emulsions stabilized with different surfactant or different volume fraction. As stated before, this normalization is equivalent to eliminating the effect of the radius, interfacial tension and volume fraction on the absolute value of the elastic modulus (see Eq. (1) and Fig. 4b). With this normalization only dynamic effects should remain. These effects would be the Gibbs elasticity and the relative rate of deformation to change in particle interaction. The slope of this representation is higher at the lower volume fraction while the dependence on the nature of the surfactant is not clear. For a volume fraction equal to 0.75 the slope for the emulsion stabilized with SDS is higher than for the emulsion stabilized with the polymeric surfactant while for the volume fraction of 0.69 the opposite is true. If Gibbs elasticity was responsible for this effect one would expect to consistently have a higher slope for the polymeric surfactant. On the other hand, a volume fraction dependence would not be expected. If the change in the rate of deformation of the interfaces compared with the change in interdroplet interaction is the cause of this effect one would expect to have a larger effect at low volume fraction. This agrees with a mechanism in which the elasticity at a low volume fraction is due to the change in interparticle distance and at a high volume fraction to the bending of the interfaces while for intermediate volume fractions both contributions exist and their relative importance depends on the frequency. At high frequency the elasticity would be due to both contributions while at low frequency only the interparticle contribution would be important. This agrees with the rheological behavior of mixtures of emulsions and suspensions [11]. At low volume fraction, below 0.6, both emulsions and suspensions behaved in the same way (this means that deformation was unimportant). Above this volume fraction the rheology was highly different with moduli that increased exponentially with volume fraction for the solids and linearly for the droplets [11]. For emulsions prepared with SDS and a dispersed phase volume fraction of 0.98 the linear viscoelastic region extends up to strains of 0.03–0.05 and does not show any dependence with frequency in the range of 10^{-3}–10 Hz, this was the case for nonionic highly concentrated w/o emulsions as well [15].

Concerning the viscous modulus, G'', in Figs. 2 and 3 the increasing role of the viscous modulus in the rheology of the system as the concentration is decreased can be appreciated. At very low volume fractions, below the onset of elasticity (parameter b in Eqs. (1) and (2)), the emulsions show a predominantly viscous behavior. This indicates a transition from a high-interaction system to a low-interaction system when the volume fraction below the limit for the droplets to be undeformed. Below this limit the system can relax in a more efficient way and elasticity is only found in the higher-frequency region.

Conclusions

A synergistic effect was found with mixtures of anionic and macromolecular nonionic surfactants on emulsion droplet size and stability. The interfacial tension γ of the mixtures is dominated by the adsorption of the anionic surfactant with γ values reaching the equilibrium value quite rapidly, the polymeric surfactant dominates the transient behavior. The rheology of the emulsions was primarily influenced by the emulsion droplet size, equilibrium interfacial tension and volume fraction. The nature of the surfactant is only clearly observed in the extent of the linear viscoelastic region and for emulsions at the onset of close packing. This agrees with emulsion droplet deformation as the main contribution to emulsion elasticity for emulsions above the onset of close packing and interparticle interaction below this limit.

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