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Surface tension and rheology of aqueous dispersed systems containing a new hydrophobically modified polymer and surfactants

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Abstract

This article reports data supporting that the hydroxypropyl cellulose-methyl methacrylate (HCMMA) hydrophobically modified polymer studied is surface-active at the air–water interface due to its amphiphilic nature. Surface tension measurements of diluted solutions point to the formation of a complex between this copolymer and a polyoxyethylene nonylphenyl ether non-ionic surfactant of high HLB. Conversely, no indications of specific interactions were found either with a polyoxyethylene nonylphenyl ether non-ionic surfactant of intermediate HLB or with an anionic surfactant such as sodium dodecyl sulfate (SDS). The physical stability of such dispersions depended on the surfactant used. The HCMMA/SDS systems studied showed phase separation shortly after preparation, while the dispersions with the non-ionic surfactant of higher HLB exhibited at least short-term stability and Newtonian behaviour. Foam-like dispersions of HCMMA–surfactant systems with intermediate HLB presented long-term stability, underlying the important role of hydrophobic interactions in these systems. One of the latter dispersions and the corresponding continuous phase were rheologically characterised by small amplitude oscillatory shear and flow curve experiments and exhibited a high Newtonian viscosity up to a critical shear stress followed by a shear thinning as well as weak-gel viscoelastic properties. The results obtained support that (a) the continuous phase presents a complex microstructure, which required the use of a serrated sensor system to avoid the occurrence of wall depletion phenomena, (b) it controls the rheology of the whole dispersion and (c) the latter showed both physical stability and rheological properties suitable for applications as controlled release systems in pharmacy or cosmetics.

Keywords: Hydroxypropyl cellulose-methyl methacrylate; Surfactants; Sodium dodecyl sulfate; Polyoxyethylene nonylphenyl ether; Surface tension; Rheology

1. Introduction

A hydrophobically modified polymer (HMP) is a water-soluble polymer, onto which short hydrophobic side-chains have been grafted (Piculell et al., 1996). If the hydrophobicity of the polymer is relatively high, the interactions with surfactants can be enhanced to modify their polimers' rheological properties. Interestingly, many properties of HMP, such as their thickening, gelling, foaming and emulsifying properties can be changed by the addition of surfactants. An added surfactant will interact strongly with the hydrophobic group of the polymer, leading to a strengthened association between polymer chains and thus to an increased viscosity (Holmberg et al., 2002). For instance, Goddard and Ananthapadmanabhan (1998) established that the interaction of a non-ionic polymer such as polyethyleneoxide (PEO) or polyvinylpyrrolidone (PVP) with an anionic surfactant such as sodium dodecyl sulfate (SDS) manifests itself as a significant increase in viscosity at a certain surfactant concentration, independent of polymer molecular weight. Furthermore, interactions of the oxyethylene groups of non-ionic surfactants with polyacrylate polymers have been reported to lead to alterations in viscosity. For instance, marked increases in viscosity of hydrophobically modified polyacrylate polymers were described by Sarrazin-Cartalas et al. (1994) in the presence of non-ionic surfactants.

Two important concepts which must be clearly distinguished when dealing with polymer–surfactant systems are the critical aggregation concentration (CAC) and the critical micelle

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concentration (CMC). The latter corresponds to a narrow surfactant concentration range at which individual surfactant molecules self-aggregate to form dynamic entities called micelles (Panmai et al., 1999). Surfactant micelles may be spherical, rod-shaped, or disk-like depending on intra-micellar and inter-micellar interactions (Israelachvili, 1985). On the other hand, the CAC is the surfactant concentration at which interactions between polymer and surfactant start to be apparent as a consequence of the formation of a complex between them. Such concentration turns out to be lower than the CMC of the corresponding surfactant/water system (Hormnirun et al., 2000).

Rodenhiser and Kwak (1998) determined the CAC of SDS and several polymers (PEO and PVP) by surface tension measurements. Binding of SDS to polymers was explained by a hydrophobic bonding mechanism similar to micelle formation. Several studies (Dualeh and Steiner, 1990; Biggs et al., 1992; Magny et al., 1994; Piculell et al., 1996) have shown that the hydrophobes of HMP induce a specific aggregation of surfactant micelles around these hydrophobic groups at concentrations below the CAC of unmodified polymers, such as hydroxyethylcellulose. The strength of hydrophobic interactions is enhanced by the bridging of hydrophobic domains with surfactant micelles, resulting in an increase in the solution viscosity and even leading to gelation. Therefore, interactions between HMP and surfactants depend on both the number of hydrophobes to the number of surfactant micelles (stoichiometry:ratio of bound surfactant to HMP hydrophobe) and on the strength of the interactions between the hydrophobic groups and the surfactant (Panmai et al., 1999). These interactions involve forming a mixed micelle, the surfactant tail length and that of the hydrophobic groups influencing the strength of such interactions. Several studies have shown the close analogy between HMP–surfactant associations and the mixed micellisation of surfactants. The HMP hydrophobes may be considered the fundamental units of the HMP, since they are responsible for the strong association phenomena observed (Piculell et al., 1996).

The addition of surfactants to polymers has been found to exert a dramatic effect on the rheological properties as a consequence of hydrophobic interactions between lipophilic tails of surfactants and the corresponding region of polymers (Thuresson and Lindman, 1997). Shear flow experiments carried out under well-defined geometries provide fundamental information on the flow properties of these systems (Whorlow et al., 2005).

A new generation of copolymers constituted by semi-synthetic (cellulose derivatives) and synthetic (methacrylates) polymers have been recently introduced as excipients for oral controlled-release matrices (Castellano et al., 1997a; Ferrero et al., 1997, 2003).

Since hydroxypropyl cellulose-methyl methacrylate (HCMMA) is a HMP, the aim of this work was to determine the possible interactions between this HMP (HCMMA) and different (anionic and non-ionic) surfactants as well as to explore the formation of stable dispersed systems which could be used as topical dosage form in pharmaceutical applications.

2. Materials and methods

2.1. Materials

The HMP used was a hydroxypropyl cellulose-methyl methacrylate synthesized as detailed in a previous work (Castellano et al., 1997a,b). The monomer methyl methacrylate (MMA) was grafted on a cellulose derivative (hydroxypropyl cellulose) by free radical polymerisation, using Ce (IV) as initiator. The product HCMMA obtained was dried in a vacuum oven (5–10 mmHg) at 50 °C until constant weight.

The non-ionic surfactants used were a commercial polyoxyethylene (EO = 100) nonylphenyl ether (Igepal CO990®, hydrophilic–lipophilic balance (HLB) 19, Mw 4626, batch 12029EY) and polyoxyethylene (EO = 5) nonylphenyl ether (Igepal CO520®, HLB 10, Mw 441, batch 17812LO). The anionic surfactant was a sodium dodecyl sulfate (HLB 40, Mw 288.38, batch 454338-1). All the surfactants were used as received, without any further purification, and were purchased from Sigma–Aldrich, Barcelona, Spain.

2.2. Surface tension measurements

The Wilhelmy plate technique (KSV digital tensiometer, model Sigma 701. KSV Instruments Ltd.) was used to measure the surface tension. Measurements were conducted in duplicate at temperature 25 ± 0.1 °C and at atmospheric pressure.

Surface tension was firstly determined for HCMMA copolymer (0.6×10^{-4}–3×10^{-4} wt.%) solutions. The HCMMA was previously diluted in toluene (0.012 wt.%) and then spread on the deionised water surface. Secondly, surface tensions of the surfactant solutions were also determined in a concentration range from 8.64×10^{-7} to 5.19×10^{-5} M for Igepal CO990®, from 9.07×10^{-7} to 2.72×10^{-4} M for Igepal CO520® and from 1.39×10^{-7} to 4.16×10^{-2} M for SDS. Thirdly, the surfactant solutions were placed in the tensiometer cell and 500 μl of the toluene solution (6×10^{-5} g HCMMA) was spread using a micro-syringe. In addition, 2000 μl (24×10^{-5} g HCMMA) of the toluene solution was spread on Igepal CO520® and SDS solutions. All the surfactant–HCMMA systems were allowed to equilibrate overnight.

2.3. Preparation of dispersions and determination of physical stability

Concentrated aqueous dispersions of the HCMMA/surfactant systems were prepared with an Ultra-Turrax T18 homogeniser equipped with an S-18 N-19 G turbine (IKA, Staufen, Germany). Homogenisation was carried out at 6000 rpm and the beaker containing the sample was kept in a circulator bath at 30 °C for the batch operation time (2 h). The detailed procedure consisted of adding the required amount of HCMMA on the previously prepared aqueous solution of the corresponding surfactant. This composition range was fixed after conducting preliminary experiments to locate the surfactant and HCMMA concentrations at which possible candidate dispersed systems to be used as topical dosage form exhibited a reasonable consistency.

Table 1
Composition of the HCMMA/surfactant/water systems (wt.%) used for the rheological study

Surfactant		HCMMA	Water
Igepal CO990®	30	1.4	68.6
	33	1.5	65.5
	35	1.6	63.4
	40	1.7	58.3
Igepal CO520®	25	1.5	73.5

Phase separation was checked by visual inspection when a supernatant low-viscous liquid appeared above a gel-like phase.

2.4. Rheological characterization

The samples used to carry out the rheological study were prepared by following the same method as explained above for the phase separation study. The samples were allowed to rest at room temperature for 24 h after their preparation before conducting any rheological test in order to ensure the same recent shear history for all the samples and to avoid mechanical memory effects. The rheological study was only undertaken for samples which did not show phase separation 24 h after preparation. The compositions of the HCMMA/surfactant systems studied are shown in Table 1.

The HCMMA/Igepal CO520®/water systems studied could be considered as foam-like dispersions, insofar as air bubbles were randomly distributed in a viscous matrix. A further objective was to gain a deeper insight in the system which exhibited the best physical stability behaviour by studying the rheology of its continuous phase. This turned out to be the dispersion containing Igepal CO520®. Centrifugation at 3500 rpm for 1 h was used to remove air bubbles from the dispersion and to obtain the corresponding continuous phase.

Multi-step flow curve measurements were run using a controlled-stress rheometer, RS-100 (Haake, Karlsruhe, Germany), using plate & plate sensor systems of 60 mm diameter with smooth (PP 60) and serrated (PP 60 R) surfaces for dispersions containing Igepal CO520®. The experimental protocol consisted of applying every shear stress either until an approximation to the steady-state of 0.001 was reached or until a maximum time of 300 s per point. Flow curves of dispersions with Igepal CO990® were determined with a cone and plate geometry (diameter: 35 mm, angle: 1°) by using the controlled-rate mode of the rheometer (AR 1000. TA Instruments) on account of their Newtonian behaviour.

Small amplitude oscillatory shear experiments were carried out in the RS-100 rheometer to determine the linear dynamic viscoelastic properties of selected samples. The PP 60 R sensor was used for these tests. First of all, the linear viscoelastic region for the different systems was determined by stress sweeps at 0.3, 1 and 3 Hz. A stress amplitude of 2 Pa was used to determine the mechanical spectra in a frequency range from 0.1 (0.628 rad/s) to 4.8 Hz (30.14 rad/s). The analysis of results is based on the storage (G') and loss (G'') moduli, which are related to the elastic and viscous component, respectively. All measurements were made at 25 ± 0.1 °C and vaseline oil was used as sealing agent to prevent samples from drying-out. Each measurement was made in triplicate. The sensor systems used in this work were calibrated with SUA1 standard fluid (Hudson and Jones, 1993).

3. Results and discussion

3.1. Surface tension measurements

The surface tension measurements performed on diluted solutions have been employed in this study to determine the possible interactions that may exist at the air–water interface between surfactant and HCMMA molecules.

The surface characterization of polymeric dispersions has some practical difficulties. First of all, measurements have to be done once the equilibrium has been reached and usually this requires a long experimental time, especially for high molecular weight species. This is due to the facts they diffuse slowly to the interface and that once adsorbed the further molecular reorganisation at the interface is also a slow process. Furthermore, the polymer concentration required in the solution phase to get a full surface coverage is usually rather low. In addition, when polymers are water-insoluble as in this case, measurements have to be done by spreading first the polymer molecules from a carrier solvent, which must be volatile.

Fig. 1a shows the surface tension of spread HCMMA on water. Surface tension markedly dropped with HCMMA concentration up to roughly 1.7×10^{-4} wt.% and levelled off above such a critical value about 58.5 mN/m. These results indicate that the copolymer by itself is surface active at the air–water interface, as a result of its amphiphilic nature. While the cellulose groups are hydrophilic, the methyl methacrylate groups are responsible for the hydrophobic properties of the copolymer.

It is well known that surface tension results of surfactant solutions are characterised by a distinctive break with respect to the surfactant concentration, which is associated with the formation of supramolecular aggregates (micelles) at the so-called critical micelle concentration (Rana et al., 2002).

The concentration dependence of the surface tension of aqueous solutions of the Igepal CO990® (HLB 19) is shown in Fig. 1b Surface tension markedly decreased with concentration as surfactant molecules adsorbed at the air–water interface until saturation is reached as indicated by a plateau in the plot of surface tension versus concentration. Such plateau is due to the equilibrium between molecules at the interfacial surfactant monolayer and in the bulk solution. Fig. 1b illustrates that the surface tension levelled off around 52 mN/m at a surfactant concentration of ca. 1.4×10^{-5} M. This critical concentration is the CMC for aqueous solutions of Igepal CO990® and was estimated from the break point. Fig. 1b also shows that the addition of copolymer resulted in a drop of surface tension when compared with the surfactant solution data. These results may be attributed to the binding of surfactant and copolymer molecules, which leads to a CAC (T_1) value around 5.19×10^{-6} M of Igepal CO990®. This value was lower than the CMC of Igepal CO990®, consistently with results reported for other systems (Hormnirun et al., 2000). For the interaction of surfactants with

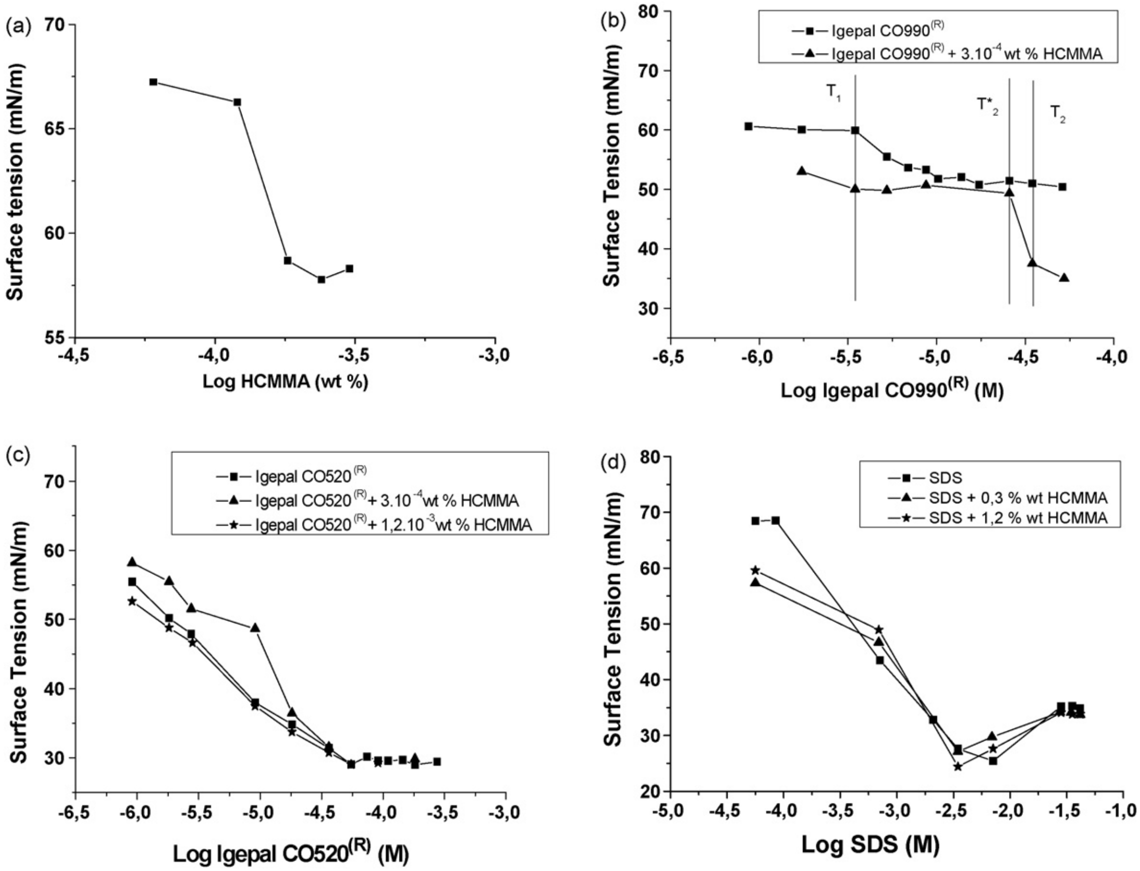

Fig. 1. Surface tension vs. concentration at 25 ± 0.1 °C. (a) HCMMA spread on water surface (b) Igepal CO990® alone and with 3×10^{-4} wt.% of HCMMA (c) Igepal CO520® alone and with 3×10^{-4} wt.% and 1.2×10^{-3} wt.% of HCMMA. (d) SDS alone and with 3×10^{-4} wt.% and 1.2×10^{-3} wt.% of HCMMA.

non-ionic polymers, it is a general observation that anionic surfactants interact strongly with neutral polymers, cationic surfactants much less so, and it is the exception rather than the rule when non-ionic surfactants interact with non-ionic polymers (Couderc-Azouani et al., 2005). For that reason, the CAC (T_1) is an indication of the beginning of the cooperative surfactant aggregation to the polymer. The greater the difference CMC–CAC is, the higher is the affinity of the surfactant for the copolymer. For concentrations below T_1, surface tension decreases because all the added surfactant partitions between the solutions bulk as a monomer and the air–water interface, where the copolymer is also present. In the composition range T_1–$T_2{}^*$ surface tension is constant. This is an indication that all the added surfactant aggregates on the copolymer while the composition at the air-solution interface does not vary. The presence of a defined plateau in the surface tension data is more compatible with the copolymer saturation mechanism than with the formation of mixed micelles. In the $T_2{}^*$–T_2, the surface tension decreases again because the Igepal CO990® concentration increases as monomer in the bulk as well as the air–water interface (Otorna et al., 2006; Taylor et al., 2007).

Fig. 1c shows the surface tension values of Igepal CO520® solutions in the absence or not of HCMMA. The CMC of the Igepal CO520® water solution was around $5.4\,10^{-5}$ M, in agreement with literature data (Porter, 1991a,b). The surface tension values of the Igepal CO520® (HLB 10)–HCMMA (3×10^{-4} wt.%) system was similar to those of the surfactant solution in contrast to the results obtained with Igepal CO990® (HLB 19). A further increase in the HCMMA concentration to 1.2×10^{-3} wt.% did not influence the surface tension values. This clearly indicates the lack of interactions between this surfactant and the HCMMA, probably because the affinity of the surfactant for the interface air–water is major than that of the hydrophobically modified polymer. Therefore, the air–water interface is just saturated by surfactant molecules, whose arrangement in the interface is not affected either by the presence of the copolymer in the bulk solution.

The equilibrium surface tension of the water solution of the Igepal CO520® was significantly lower than the corresponding value for Igepal CO990®. This may be attributed to the lower average molecular weight or better the lower average molecular size of the former, which probably resulted in a higher number of Igepal CO520® molecules in the interface (Leibler et al., 1983). Besides, the different results obtained with both non-ionic surfactants must be attributed to the substantial difference in the number and area of polyoxyethylene moiety (Boissier et al., 2001) and, as a consequence, in their respective HLB. In accordance with the results reported by Porter (1991a,b), the equilibrium surface tension goes down with the decrease in the ethoxylation degree.

In general, there is little or no interaction between non-ionic polymers and non-ionic surfactants (Taylor et al., 2007).

Fig. 1d illustrates the influence of SDS concentration on the surface tension of their aqueous solutions and also of SDS solutions where the HCMMA had been spread on the air–water interface. The experimental CMC of SDS aqueous solutions was ca. 8×10^{-3} M, in agreement with data available in the literature (Ottewill, 1984; Porter, 1991a,b; Vaknin et al., 2004). The SDS water solutions exhibited a higher CMC than those obtained for the non-ionic surfactants studied, owing to the strong electrostatic repulsions between the charged head groups (Williams, 2003). Fig. 1d also shows that a rise in HCMMA concentration up to 1.2×10^{-3} wt.% did not significantly influence the surface tension of the SDS/water solution, indicating the lack of interactions between SDS and HCMMA molecules in the interface. Similarly to the interpretation proposed for Igepal CO520®/HCMMA/water systems, the arrangement of SDS molecules at the interface was not significantly altered either by the presence of copolymer molecules in the interface or in the bulk solution.

3.2. Physical stability of HCMMA/surfactant/water dispersions

The phase behaviour of polymer/surfactant/solvent systems has been found to be similar to that of solvent/mixed polymer systems. Phase separation may occur by the formation of two liquid layers, one rich in the polymer and the other rich in the surfactant (Williams, 2003).

An outline of the phase diagram of the Igepal CO990®/HCMMA/water system after 24 h of preparation is shown in Fig. 2a in the range of concentrations used to prepare dispersions exhibiting a suitable consistency to be used as topical dosage form. Fig. 2a shows a region of apparent monophasic systems above the line drawn, which located the boundary of a composition range where phase separation occurred by 24 h after sample preparation. The term apparent monophasic system has been used to note that eventually phase separation took place after 7 days of sample preparation. Phase separation occurred by the formation of two layers, with a supernatant low-viscous liquid above a gel-like phase. A similar behaviour was found by Maestro et al. (2005) when studying interactions of surfactant–copolymer systems likely to be used in the formulation of waterborne paints.

Fig. 2b displays the corresponding outline of the phase diagram of Igepal CO520®/HCMMA/water system again in the composition range which guaranteed the formation of dispersions with the right consistency to be used as topical dosage form. The key difference with the Igepal CO990® system is that dispersions located above the boundary line exhibited a long-term physical stability (more than 30 days). In addition, at the higher HCMMA weight percentages the concentrations of non-ionic surfactant required to form dispersions exhibiting long-term stability were clearly lower for Igepal CO520® system than for those containing Igepal CO990®. The results obtained seem to indicate the occurrence of a better compatibility between the HCMMA, which is more hydrophobic than hydrophilic according to its low solubility in water and the non-ionic surfactant with the lowest HLB. This emphasises the important role of hydrophobic interactions in these systems.

The dispersions obtained with the HCMMA/Igepal CO520®/water system showed the appearance of a wet or spherical foam. Wet foams are generated by agitation in order to prepare concentrated aqueous solutions of these polyoxyethylene surfactants (Herzhaft, 2002; Schulte and Höfer, 2003).

As far as the systems containing the anionic SDS surfactant are concerned, it was not possible to obtain HCMMA/SDS/water systems with some physical stability along the whole HCMMA concentration range tested. This fact may be explained by considering that SDS was the most hydrophilic surfactant studied in this work and is consistent with the previous interpretation proposed for the non-ionic surfactants.

3.3. Rheological characterization

The main target of the rheological study was to study samples likely to be used as topical dosage forms and exhibiting homogeneous macroscopic properties. The physical stability study revealed that above the boundary line (Fig. 2b) of the HCMMA/Igepal CO520®/water system, the existence of

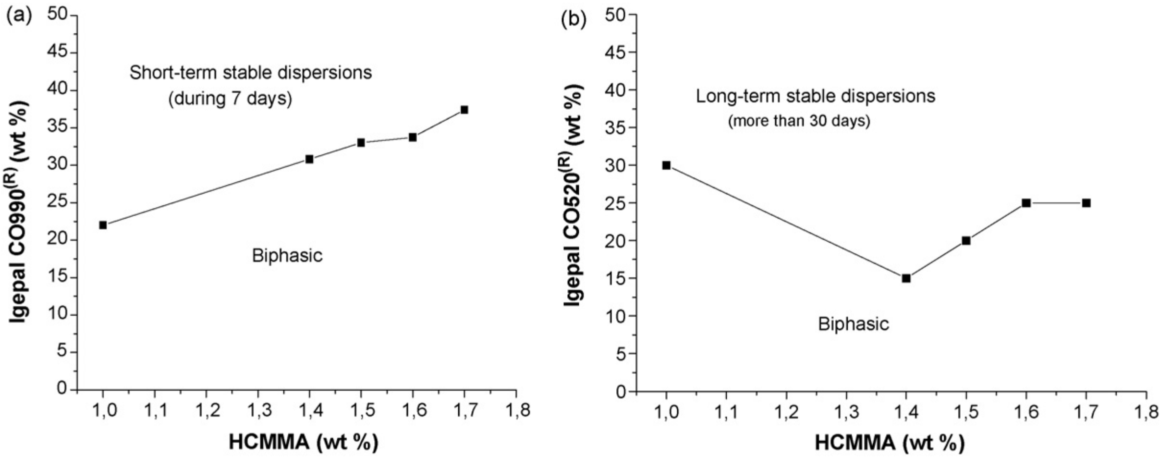

Fig. 2. Outline of the phase diagram at 25 ± 0.1 °C. (a) HCMMA/Igepal CO990®/water dispersions and (b) HCMMA/Igepal CO520®/water dispersions.

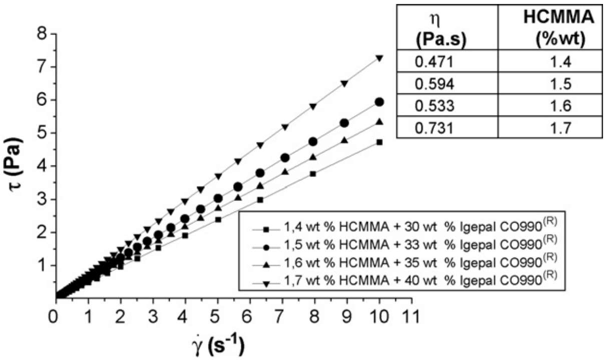

Fig. 3. Flow curves and Newtonian viscosity (η) of HCMMA/Igepal CO990®/ water systems at 25 ± 0.1 °C.

samples which fulfilled the above mentioned requirements was readily guaranteed. Yet, foam-like dispersions exhibiting long-term physical stability were formed, which despite being inherently heterogeneous, could be considered as "homogeneous" at the size scale of the sensor system chosen to do the rheological measurements. Given that no problems were found concerning the physical stability of these samples, only one composition was chosen for the rheological study. Upon fixing a concentration of 1.5 wt.% HCMMA, the corresponding minimum weight percentage of Igepal CO520® required to be well within the composition region guaranteeing long-term stability was 25wt.%.

A further step of the rheological study dealt with samples whose compositions were located, in the apparent (7 days) monophasic region of the HCMMA/Igepal CO990®/ water system, as close as possible to the boundary line limiting the realm of existence of dispersions which showed clear phase separation in 24 h after preparation. The compositions of the samples studied ranged from 1.4 to 1.7 wt.% HCMMA and from 30 to 40 wt.% Igepal CO990®.

Fig. 3 shows that all the dispersions studied containing Igepal CO990® exhibited flow curves typical of Newtonian systems, as the viscosity was independent of shear rate. The values of Newtonian viscosity are shown in the same figure.

The flow curve of the foam-like HCMMA/Igepal CO520®/ water dispersion turned out to be quite different to those of the dispersions containing Igepal CO990®. Fig. 4a, shows an apparent non-Newtonian zone up to 10 Pa with an apparent zero-shear viscosity higher than 2×10^5 Pa s (i.e. higher than 200×10^6 times the viscosity of water at 20 °C). This means that the Newtonian viscosity of the dispersion containing Igepal CO520® was five orders of magnitude higher than the corresponding values of dispersions with Igepal CO990®. Dispersion with Igepal CO520® exhibited non-Newtonian shear thinning behaviour above 10 Pa. The rheological measurements of these foam-like dispersions were conducted with great care, since they were likely to present slip or better wall-depletion phenomena. These basically consist of displacement of the disperse phase away from the solid surface of the sensor system, due to either static (or better geometric) effects or dynamic, i.e. shear induced effects (Barnes, 2000). This yields a depleted layer of liquid which then acts as a lubricant and consequently leads to an apparent decrease in the measured bulk viscosity (Barnes, 1995). For this reason, a serrated plate & plate sensor system was used to reduce the risk of wall depletion (Franco et al., 1998).

Given the high viscosities exhibited by the dispersion containing Igepal CO520®, a further step was to determine the contribution of its continuous phase. This was obtained after centrifugation, on account of the different densities of the gas (air) and the semi-fluid continuous phase (Schulte and Höfer, 2003). The flow curve of the continuous phase is also plotted in Fig. 4a and was run following the same experimental protocol as that used for the foam-like dispersion to guarantee a strict comparison. Therefore, the serrated plate–plate geometry was also chosen to study the flow properties of the continuous phase. Its apparent low-shear Newtonian viscosity (~1×10^5 Pa s) turned out to be lower than the value exhibited by the foam-like dispersion (~2×10^5 Pa s), although both were of the same order of magnitude. Furthermore, the apparent critical shear stress for the onset of non-linear (shear thinning) response was around 10 Pa for both systems. However, the shear thinning properties of the foam-like dispersion were more marked than for its continuous phase, due probably to the additional effect of the disruption of bubbles under shear in the former. On the whole, the flow behaviour of the foam-like dispersion was essentially controlled by its continuous phase, which therefore may be used as a simpler model than the dispersion.

In order to gain a deeper insight into the properties of the continuous phase, further flow curve experiments were conducted using a smooth surface parallel plate sensor system and varying the gap, i.e., the sample thickness (Fig. 4b). Interestingly, the apparent Newtonian viscosity at low shear stress increased with the gap size and the data obtained at the higher shear stresses were rather noisy. These results point to the occurrence of wall depletion also in the continuous phase of the dispersions. Slip effects in apparently homogeneous systems such as polymer dispersions have been attributed to the occurrence of microaggregates, like microgels (Aubry et al., 2000) The dispersions studied in this work exhibited distinctive microcrystalline fractions when observed under polarising microscopy, which may be responsible for the wall depletion observed under shear. This fact was confirmed by comparing the flow curves obtained using the same experimental protocol with a smooth surface and a serrated plate and plate sensor system with a gap of 1 mm (Fig. 4c). As expected, the results obtained with the smooth surface parallel plate geometry underestimated not only the viscosity values but also the critical shear stress for the onset of shear thinning response. Similar rheological features were reported by Franco (Franco et al., 1998; Gallegos and Franco, 1999) for different types of emulsions. The shear thinning properties of the continuous phase may be associated with the orientation of polymer–surfactant aggregates and also to the partial disruption of microcrystalline domains.

Another important point of the rheological characterization of any complex fluid deals with its viscoelastic properties. The foam-like dispersion containing 1.5 wt.% HCMMA and 25 wt.% Igepal CO520® as well as its continuous phase were studied by small amplitude oscillatory shear (SAOS). These dynamic viscoelastic experiments allow the characterization of a material

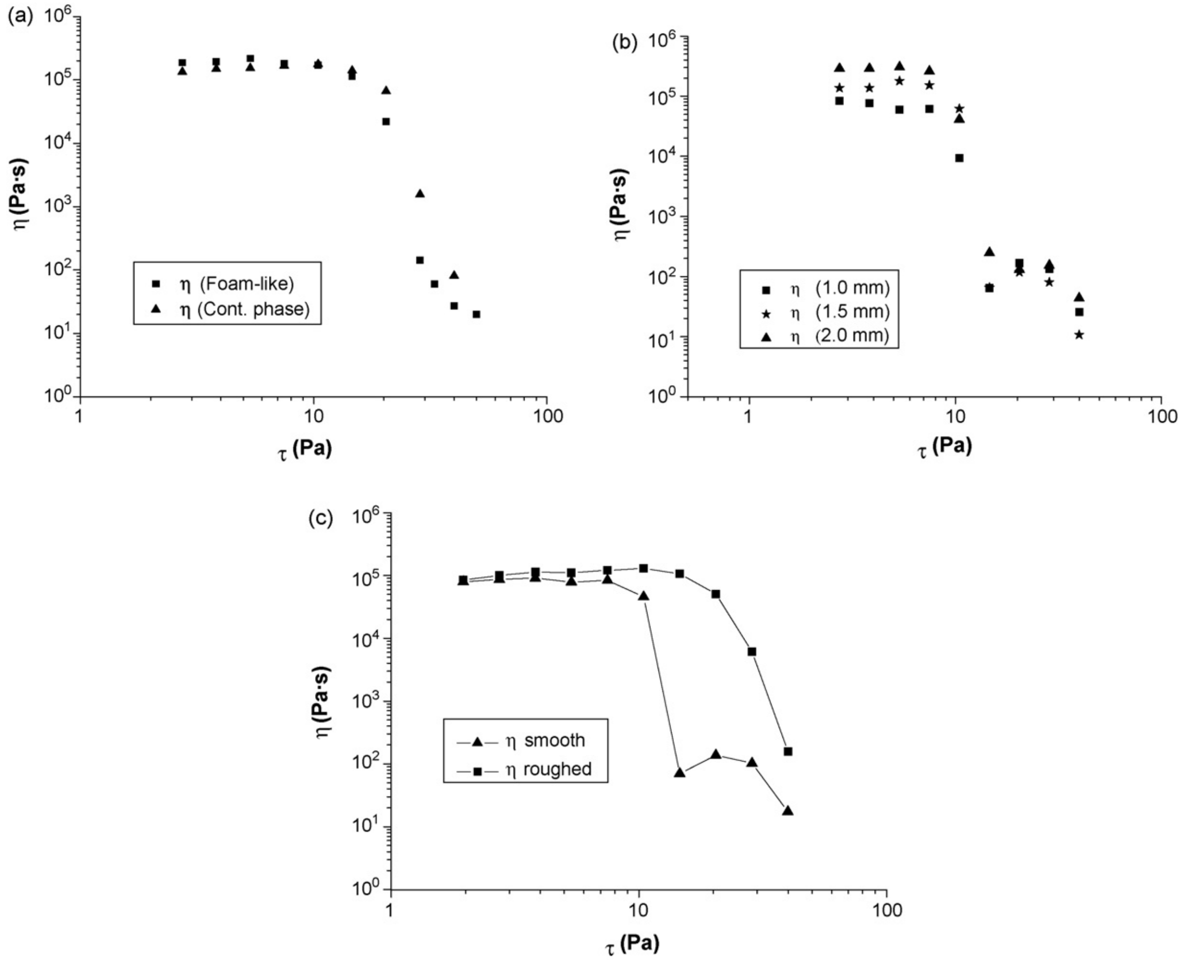

Fig. 4. Viscosity versus shear stress of HCMMA/Igepal CO520® system at 25 ± 0.1 °C: (a) the foam-like and of its continuous phase. (b) The continuous phase of system at different gap sizes (c) the continuous phase of the system with different sensors.

without irreversibly altering its static structure (Lippacher et al., 2001). SAOS provides information on the viscous and elastic components of the viscoelastic response as well as indirect information on the relaxation spectrum, which is closely related to the network structure of complex dispersed systems.

The first step of the experimental protocol used was to conduct stress sweeps under oscillatory shear at fixed frequency to estimate the limit of the linear viscoelastic response. As a rule, this type of experiment is usually carried out at 1 Hz; however we repeated the stress sweeps using three frequencies (0.3, 1 and 3 Hz) in order to check that the shear stress amplitude guaranteed a linear viscoelastic response along the whole frequency sweeps experiments. Fig. 5 illustrates that the critical shear stress for the onset of non-linear viscoelastic behaviour may depend on frequency, hence the value chosen to determine the mechanical spectra must be well below the critical value. In addition, Fig. 5 clearly demonstrates that the storage (G′) and loss (G″) moduli values of either the foam-like dispersion or its corresponding continuous phase were not significantly different when compared at the same frequency and that the influence of frequency did seem to be rather weak. This was confirmed by frequency sweep results (Fig. 6). The storage modulus was always higher than the loss modulus, therefore the dispersed system was more elastic than viscous in the frequency range investigated. Both parameters showed a weak dependence on the applied frequency, as expected, indicating a gel-like behaviour (Alfaro et al., 2000). The scarce differences found between the dispersion and its continuous phase fall within the typical exper-

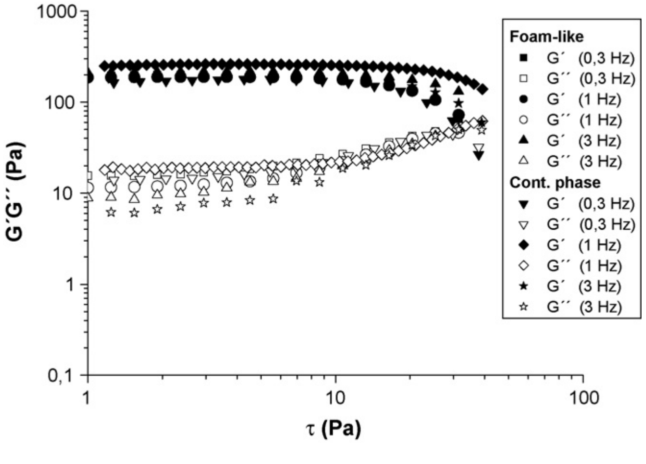

Fig. 5. Storage (G′) and loss (G″) moduli of the foam-like dispersion and its continuous phase containing HCMMA/Igepal CO520® at 25 ± 0.1 °C.

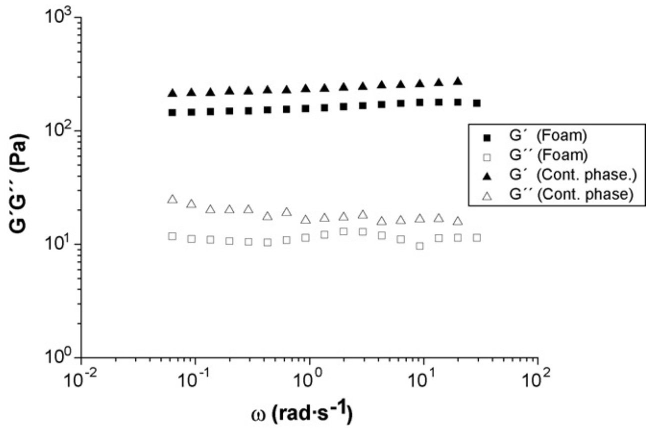

Fig. 6. Oscillation frequency sweep of the foam-like dispersion and its continuous phase containing HCMMA/Igepal CO520® at 25 ± 0.1 °C.

imental errors of small amplitude oscillatory shear tests. The results obtained confirmed that the continuous phase controlled the linear viscoelastic response of the foam-like dispersion, as a consequence of its decisive contribution to the whole structure.

4. Conclusions

Surface tension results of diluted aqueous solutions of the hydroxypropyl cellulose-methyl methacrylate copolymer studied demonstrated it is surface-active on account of its ability to drop the surface tension to equilibrium value of 58.5 mN/m. In addition, they support the occurrence of a complex between HCMMA and Igepal CO990® non-ionic surfactant (HLB 19), characterized by a CAC of about 5.2×10^{-6} M, which may be responsible for the synergistic fall in surface tension observed. Conversely, they did not support the existence of specific interactions in the air–water interface of HCMMA with either Igepal CO520® (HLB 10) non-ionic surfactant or SDS (HLB 40) anionic surfactant.

Concentrated aqueous dispersions of HCMMA/surfactant systems were formulated in a composition range guaranteeing a suitable consistency to find potential applications as topical dosage forms in pharmacy. HCMMA/SDS system underwent phase separation 24 h after preparation, while system HCMMA/Igepal CO990® showed a region of dispersions with short-term (7 days) physical stability. They showed Newtonian flow behaviour in the shear rate range studied. The best results were found with HCMMA/Igepal CO520® system, which presented a region of long-term (more than 30 days) foam-like stable dispersions. This suggest that a straightforward extrapolation of surface tension results of dilute solutions is hardly possible to predict the behaviour of concentrated dispersions in the composition range associated to practical applications. The 1.5 wt.% HCMMA/25 wt.% Igepal CO520® dispersion exhibited a rheological behaviour typical of weak gels. The flow curve was determined with a serrated parallel plate sensor system to avoid wall depletion phenomena. It presented an apparent Newtonian viscosity at low shear stress, which was five orders of magnitude as high as the value obtained with Igepal CO990® and shear thinning properties above a critical shear stress. Small amplitude oscillatory shear was used to characterize its dynamic viscoelastic properties, with the storage modulus (related to the elastic component) exhibiting values higher than the loss modulus (related to the viscous component) along the whole frequency range. Both viscoelastic functions exhibited weak frequency dependence as corresponds to the plateau relaxation zone. A comparison with the rheology of its continuous phase confirmed that the structure of the latter was rather complex and likely to present slip effects. Furthermore, the fact that the structure of the continuous phase controlled the linear viscoelastic behaviour of the foam-like dispersion has been clearly demonstrated. The effect of air bubbles was just apparent in the shear-thinning region of the flow curves.

This work has demonstrated that the copolymer studied, which exhibits predominant hydrophobic properties can be used to formulate long-term aqueous-based dispersions by choosing the right surfactant as well as suitable batch processing conditions.

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