

Cosurfactant effects on the polymerization of vinyl acetate in anionic microemulsion media

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Abstract

The polymerization of vinyl acetate at 60 °C in microemulsions stabilized with the anionic surfactant, Aerosol OT, with or without cosurfactant (*n*-butanol) is examined. Partial phase diagrams at 60 °C show that the addition of *n*-butanol enhances the one-phase microemulsion region. Results indicate that the reaction rate is not affected by the presence of the alcohol. However, average molar masses are smaller although particles are bigger throughout the reaction compared to those values obtained in the absence of *n*-butanol. An explanation for these results is presented.

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1. Introduction

Oil-in-water microemulsion polymerization is a unique process that allows the production with high reaction rates of high molar mass polymeric nanoparticles ($D_p < 50$ nm) dispersed in an aqueous medium [1–3]. Most investigations on this kind of polymerization have been performed in four-component microemulsions, i.e. monomer, water, surfactant and cosurfactant [4–10]. Our group reported the first polymerization in cosurfactant-free microemulsions [11]. Since then, scores of reports on the polymerization of various monomers in three-component microemulsions have been forwarded [12–20].

Even though many microemulsions are formulated with alcohols as cosurfactants, the effect of adding an alcohol on the kinetics and mechanism of microemulsion polymerization has not been systematically addressed. A few years back, Gan et al. [21] examined the polymerization of styrene in microemulsions stabilized with dodecyltrimethylammonium bromide (DTAB) and several ethoxylated alcohols as cosurfactants. They reported that the polymerization rates

and the polystyrene molar masses were affected by the molar ratio of cosurfactant to surfactant in the dispersed phase and by the type of cosurfactant. They concluded that the differences in molar mass may not be due to differences in the chain transfer constant of the alcohols but to changes in the interfacial fluidity of the particles induced by the alcohols. However, these authors did not compare their results with alcohol-free microemulsion systems. Antonietti et al. [22] polymerized styrene and methyl methacrylate in microemulsions with and without cosurfactant in order to control particle size and size polydispersity, although neither kinetic nor mechanistic comparisons were presented. Santhanalakshmi and Anandhi [23] reported the microemulsion polymerization of vinyltoluene in microemulsions stabilized with sodium dodecylsulfate in the absence or presence of various cosurfactants (*n*-alcohols and bifunctional alcohols). Again, no kinetic comparisons were presented in this paper.

Previously, we argued that the presence of an alcohol, the most common cosurfactant, was undesirable for the basic understanding of the mechanism of microemulsion polymerization because (i) they partition among the different domains of the microemulsion, (ii) they modify the partitioning of the monomer and (iii) they may act as chain transfer agents [11]. In fact, in the modeling of the

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polymerization of styrene in microemulsions containing sodium dodecylsulfate and an alcohol, El-Aasser and collaborators introduced several assumptions about the partitioning and added thermodynamic equations to satisfy equilibrium considerations due to the presence of the alcohol [7,8].

Our group recently reported the polymerization of vinyl acetate (VA) in alcohol-free AOT microemulsions; we showed there that small amounts of AOT (1 wt%) are required to stabilize microemulsions with relatively high ratios of VA/AOT (≈ 3 to 4 by weight) [20]. We found that polymerization of these microemulsions is fast and conversions near 100% are obtained in all cases producing lattices with particles smaller than 35 nm and more importantly, average molar masses and molar mass distributions (MMD) are much smaller than those typically reported for the emulsion polymerization of this monomer, especially at high conversions [24–27]. We demonstrated that chain transfer reactions to monomer are the controlling chain termination mechanism even at high conversions and argue that this might be a consequence of the small size of the reacting particles, which facilitates the exit of the monomeric radicals produced by chain transfer to monomer [20].

In this paper, the polymerization of VA in microemulsions stabilized with AOT with or without an alcohol cosurfactant (*n*-butanol or *n*-BuOH) is investigated. First, partial phase diagrams of AOT, water and VA in the absence or presence of *n*-BuOH are presented. Additionally, the kinetics of polymerization as well as both, the evolutions of particle size and the MMD, are also reported. An important result is that molar masses are smaller throughout the reaction compared to those obtained in the absence of alcohol, which suggests that *n*-BuOH acts as a chain transfer agent or facilitates the escape of monomeric radicals from the reacting particles.

2. Experimental section

Sodium bis(2-ethylhexyl)sulfosuccinate (Aerosol OT or AOT) was 98% pure from Fluka. *n*-BuOH, 99.4% pure from Aldrich, was dried for 24 h in anhydrous reactant grade MgSO_4 (Mallinckrodt) and distilled previous to use. VA (Aldrich) was distilled at 30 °C under reduced pressure and argon atmosphere, stored at room temperature in dark vials until used. The VA was stable for up to 15 days as verified by NMR. Potassium persulfate (KPS) was 99% pure from Aldrich. Water was doubly distilled and deionized.

The one-phase o/w microemulsion region was determined visually by the change from transparent to turbid of aqueous solutions of AOT or AOT/*n*-BuOH (1/1 by weight) that were titrated with VA in a thermostated water bath at 60 °C. To determine more precisely the phase boundaries, samples with compositions slightly below and above the visually determined phase boundaries were made by weight and allowed to reach equilibrium in a water bath at 60 °C.

Clear samples that did not exhibit static or streaming birefringence when examined through cross polarizers, were considered one-phase microemulsions. The phase diagram at high AOT concentrations was not examined because it is not relevant for the present study. Electrical conductivities were measured with a Jenway conductimeter at 60 °C and 1000 Hz.

A 100 mL glass reactor with magnetic stirring was employed to polymerize VA at 60 °C. The microemulsion composition was 0.97 wt% AOT or 0.97 wt% AOT/*n*-BuOH (1/1 by weight), 3.0 wt% VA and 96.03 wt% water. The concentration of KPS was 0.03 wt%. Prior to polymerization, the AOT and the AOT/*n*-BuOH aqueous solutions as well as the VA were degassed by cooling-pumping-and-heating cycles. The reacting system was continuously stirred and purged with argon during the entire reaction. Conversion was followed by withdrawing samples from the reacting system at given times and put in vials (of known weight) containing 0.5 g of a 0.4 wt% hydroquinone aqueous solution, immersed in an ice bath. Samples were then weighed and freeze-dried. Polymer weight was estimated by subtracting the known weights of AOT and hydroquinone from the total weight of the freeze-dried sample.

Particle size was measured at 25 °C and at an angle of 90° in a Malvern 4700 quasielastic light scattering (QLS) apparatus equipped with an Argon laser ($\lambda = 488$ nm). Intensity correlation data were analyzed by the method of cumulants to provide the average decay rate, $\langle I^2 \rangle (= q^2 D)$, where $q = (4\pi n/\lambda) \sin(\theta/2)$, is the scattering vector, n the index of refraction and D the diffusion coefficient. The measured diffusion coefficients were represented in terms of apparent diameters by means of Stokes law assuming that the solvent has the viscosity of water. Before QLS measurements, latexes were diluted up to 100 times to minimize particle–particle interactions and filtered through 0.2 μm Millipore filters to remove dust particles.

Freeze-dried samples for gel permeation chromatography (GPC) were washed with hot deionized water to remove most of the AOT. The dried polymer and the remaining AOT were dissolved in CHCl_3 and the polymer was precipitated with diethyl ether to remove the remaining AOT. The solid was filtered and washed with diethyl ether and vacuum dried for 5 h. The polymer was dissolved in HPLC-grade tetrahydrofuran (Merck), which was used as the mobile phase. The GPC to obtain the average molar masses and the MMD consisted of a Knauer HPLC64 pump, a Rheodyne injector (loop of 100 μL), two PL-gel MIXED-B columns (Polymer Laboratories) and a Knauer differential refractometer as a detector. All GPC measurements were calibrated with narrow polystyrene standards (Polymer Laboratories) and the molar masses were calculated with the viscosimetric equation for poly(vinyl acetate) or PVA in THF [28], $[\eta] = 3.5 \times 10^{-4} M^{0.63}$. This calibration was verified using PVA standards (Polymer Laboratories).

Measured molar masses were within 5% of the values given by the supplier.

3. Results

Partial phase diagrams of VA, water and AOT alone or mixed with *n*-BuOH (1/1 by weight) at 60 °C are shown in Fig. 1 (up to 10% surfactant or surfactant/cosurfactant mixture). In the alcohol-free system (Fig. 1A), a one-phase region (L_1) and two biphasic regions ($L_\alpha + L_1$ and ϕ_1), are detected in the water-rich corner of the diagram. The L_1 -phase, which is transparent and has low viscosity and high electrical conductivity, corresponds to the o/w microemulsion region [20]. The ($L_\alpha + L_1$) region is a dispersion of

lamellar liquid crystals. The ϕ_1 -region, which corresponds to an emulsion region, spans continuously from the water solubility of VA up to the oil side of the phase diagram [20].

For the AOT/*n*-BuOH system (Fig. 1B), only the clear, low viscosity, o/w microemulsion region, L_1 , and the biphasic emulsion region, ϕ_1 , are observed. Evidently, the incorporation of *n*-BuOH increases the o/w microemulsion region whereas the ($L_\alpha + L_1$) region vanishes within the limits investigated here, i.e. up to 30% of the mixture of AOT and *n*-BuOH (not shown).

For *n*-BuOH-microemulsions, the electrical conductivity is high (a few mS/cm) in the o/w microemulsion region and increases rapidly with increasing overall AOT/*n*-BuOH content at constant VA content. Also, the conductivity decreases with increasing VA content at each line of constant (AOT/*n*-BuOH)-to-water weight ratio (Fig. 2).

Upon polymerization, the initially transparent microemulsion becomes increasingly bluish as the reaction proceeds due to particle growth and the increasingly larger difference between the refractive indexes of water and of the growing particles. In both systems samples are milky-bluish at the end of the reaction. Conversions as a function of time for the polymerization of VA initiated with KPS at 60 °C in microemulsions containing 3% VA and 0.97% of AOT or 0.97% of an equal weight ratio of AOT and *n*-BuOH (0.485/0.485) are shown in Fig. 3. Reaction rates are fast and conversions near 100% are achieved either with AOT alone or with *n*-BuOH as cosurfactant. The evolution of conversion (Fig. 3) and the reaction rates (inset in Fig. 3) are nearly identical. In both systems, only two reaction rate intervals are observed with a maximum in reaction rate (R_{pmax}) occurring at a conversion (X_{max}) of about 20% (inset in Fig. 3). These two reaction rate intervals are typical of microemulsion polymerization [1,2].

Fig. 4 depicts the average particle size, D_p , as a function of conversion in the two systems. In the alcohol-free system, D_p remains constant up to ca. 50% conversion and then

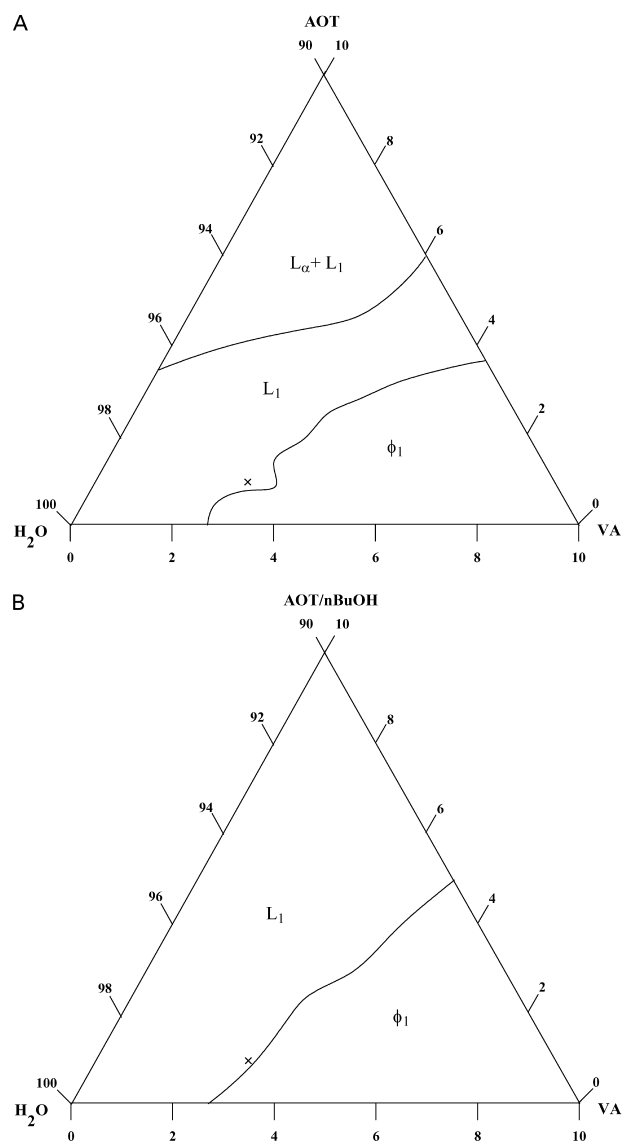


Fig. 1. Partial phase diagrams at 60 °C for the systems VA/H₂O/AOT (A, top) and VA/H₂O/AOT/*n*-BuOH (AOT/*n*-BuOH, 1/1 by weight) (B, bottom). The crosses in the phase diagrams indicate the compositions of the microemulsions that were polymerized.

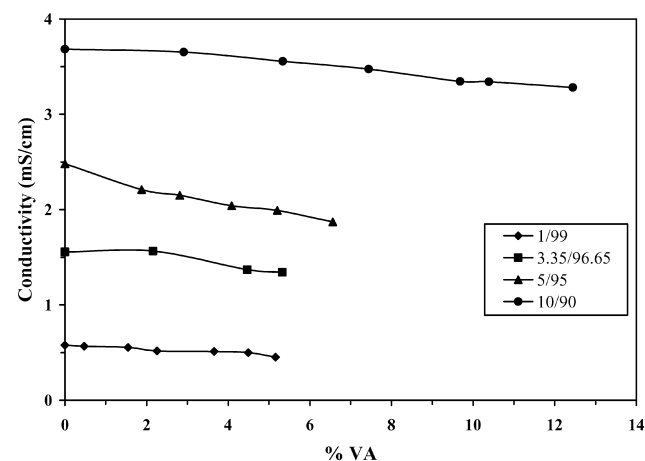


Fig. 2. Electrical conductivity at 60 °C of the o/w microemulsion region of the system VA/H₂O/AOT/*n*-BuOH as a function of VA content. The weight ratio of AOT and *n*-BuOH is equal to one but the (AOT/*n*-BuOH) to water weight ratio varies as: (♦) 1/99; (■) 3.35/96.65; (▲) 5/95; (●) 10/90.

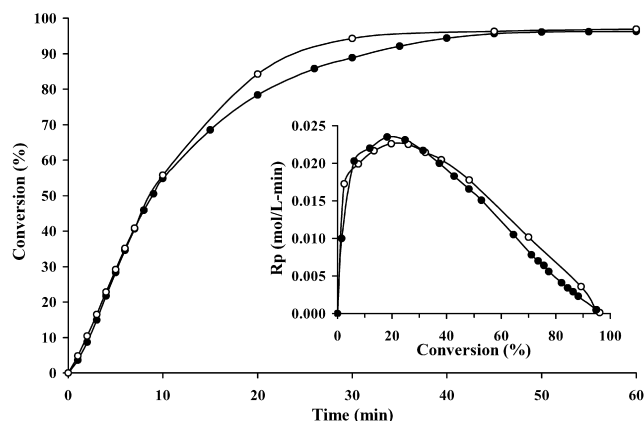


Fig. 3. Conversion as a function of time for the polymerization at 60 °C of VA (3 wt%) in o/w microemulsions stabilized with 0.97 wt% AOT (●) or 0.97 wt% AOT/*n*-BuOH (1/1 by weight) (○) initiated with 0.03 wt% KPS. Inset: polymerization rate vs. conversion for data shown in figure.

increases at higher conversions. D_p at the end of the reaction is ca. 35 nm. For the AOT/*n*-BuOH system, D_p increases continuously during the reaction and the final particle size (42 nm) is larger than the one achieved in the alcohol-free system.

With the assumptions that the particles are monodisperse with a diameter equal to that measured by QLS and that the particles are free of monomer and *n*-BuOH because of the dilution of the latexes during QLS measurements, the number density of particles, N_p , was estimated.

From these data (Table 1), it is clear that, in spite of the astringent assumptions made to estimate the number density of particles, N_p is larger in the alcohol-free system at all conversions. Also, N_p (which is zero at zero conversion) goes through a maximum in the AOT system at higher conversion ($\approx 60\%$).

Weight-average (M_w) and number-average molar masses (M_n) are shown in Fig. 5 at different conversions for both systems. Whereas M_n is constant within the GPC-experimental error and nearly identical for both systems, M_w increases with conversion. Notice that the weight-average

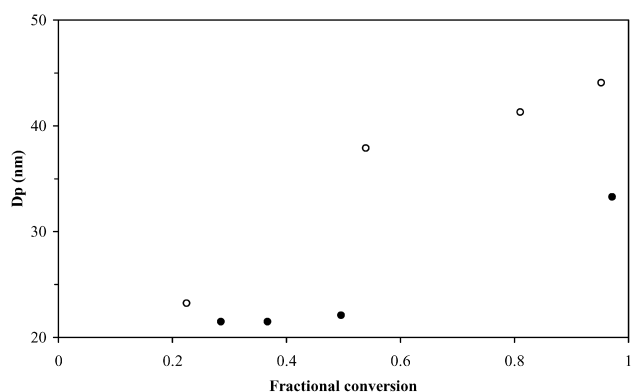


Fig. 4. Average particle size as a function of conversion for the polymerization at 60 °C of VA (3 wt%) in o/w microemulsions stabilized with 0.97 wt% AOT (●) or 0.97 wt% AOT/*n*-BuOH (1/1 by weight) (○) initiated with 0.03 wt% KPS.

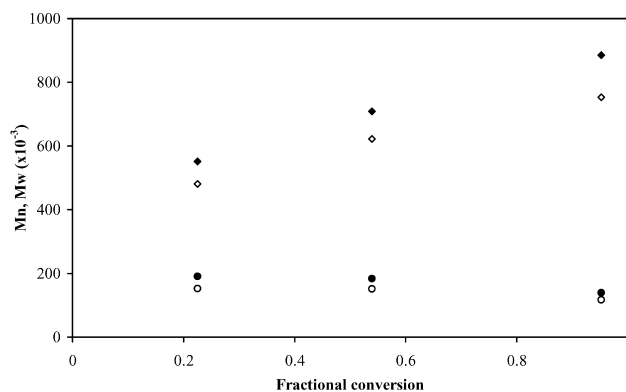


Fig. 5. Evolution of number average (M_n) and weight average (M_w) molar masses with conversion in the polymerization at 60 °C of VA (3 wt%) in o/w microemulsions stabilized with 0.97 wt% AOT (M_n : ●, M_w : ◆) or 0.97 wt% AOT/*n*-BuOH (1/1 by weight) (M_n : ○, M_w : ◇) initiated with 0.03 wt% KPS.

molar masses are larger in the alcohol-free system at all conversions.

The comparisons between the MMD of the AOT/*n*-BuOH and that of the alcohol-free systems at low and high conversions are shown in Fig. 6. At both low and high conversions, the MMD's of the alcohol-free system are skewed toward the high-molar mass population than those of the AOT/*n*-BuOH system. At low conversions only the

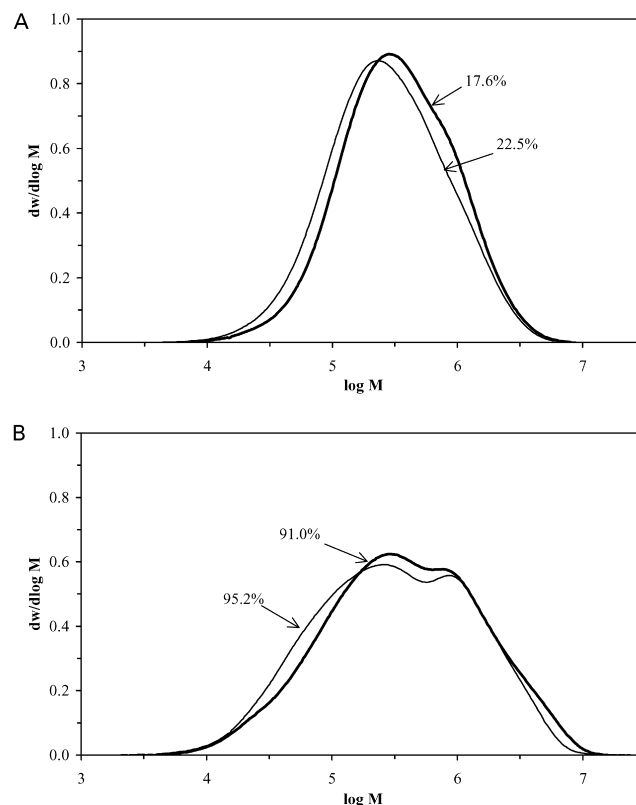


Fig. 6. Comparison between the MMD at low (A, top) and high (B, bottom) conversions during the polymerization at 60 °C of VA (3 wt%) in o/w microemulsions stabilized with 0.97 wt% AOT (—) or 0.97 wt% AOT/*n*-BuOH (1/1 by weight) (---) initiated with 0.03 wt% KPS.

Table 1

Average particle diameter (D_p) and number density of particles (N_p) in the o/w microemulsion polymerization at 60 °C of VA (3 wt%) stabilised with 0.97 wt% (AOT) or 0.97 wt% AOT/*n*-BuOH (1/1) and initiated with 0.03 wt% KPS

AOT			AOT/ <i>n</i> -BuOH		
Fractional conversion	D_p (nm)	$N_p \times 10^{-15}$ (particles/ml)	Fractional conversion	D_p (nm)	$N_p \times 10^{-14}$ (particles/ml)
0.285	21.5	1.45	0.225	23.24	9.04
0.367	21.5	1.86	0.539	37.9	8.44
0.496	22.1	2.32	0.810	41.3	6.98
0.971	33.3	1.33	0.952	44.1	5.85

alcohol-free system shows a shoulder at the high molar mass side of the distribution. However, as conversion increases a shoulder also develops in the AOT/*n*-BuOH system and the MMD's become wider and bimodal in both systems at final conversions.

4. Discussion

Aerosol OT is a double-tail anionic surfactant that forms one-phase o/w microemulsions with polar monomers such as MMA, N-methylolacrylamide (NMA), tetrahydrofurfuryl methacrylate (THFM), acrylamide (AM) and VA [12,15,20,29,30]. These monomers act as cosurfactants and place themselves at the interface creating the necessary curvature to allow the formation of o/w microemulsions. Incorporation of *n*-BuOH into the adsorbed layer of AOT and VA around the droplet reduces the electrostatic repulsion forces among neighboring molecules at the interface (reduces the thickness of the Debye double layer), minimizes the oil-water interfacial tension and decreases the persistence length of the interfacial layer (i.e. enhances its flexibility). Evidently, all these factors facilitate microemulsion formation and lead to a larger one-phase microemulsion region at expense of the lamellar phase region.

The transparency, low viscosity, high-water content and high conductivity of the VA-microemulsions containing *n*-BuOH (Fig. 2) indicate a water-continuous microstructure, i.e. oil-in-water microemulsions, similar to that inferred for the alcohol-free microemulsion [20]. As expected, conductivity increases with increasing (AOT + *n*-BuOH)/water ratio (Fig. 2). However, in contrast to conductivities reported for the system stabilized with AOT alone where the conductivity rises slightly with increasing VA content due to partial hydrolysis of this monomer [20], here conductivity decreases monotonically as the VA content increases. This behavior is similar to that observed with styrene and other non-polar monomers [11,16]. Hence, the conductivity drop due to micellar growth promoted by the presence of the alcohol overcomes the conductivity rise due to VA hydrolysis.

The polymerization of VA initiated with KPS at 60 °C in microemulsions stabilized with AOT or with a mixture of AOT and *n*-BuOH is fast and conversions near 100% are

obtained. Due to the high solubility of VA in water (2.5 wt% at 60 °C) [31], it is likely that the free radicals generated by KPS in the aqueous phase react with dissolved VA molecules to form oligoradicals as in emulsion polymerization [32]. These species grow and either they could enter microemulsion droplets to continue the reaction there or precipitate to form stable particles by adsorption of surfactant. The facts that only two reaction-rate intervals (inset in Fig. 3), which are typical of microemulsion polymerization [1,2], and that much higher molar masses than those expected from solution polymerization (Fig. 5) were observed, rule out that the reaction is carried out by solution polymerization.

The evolution of conversion is similar for the two systems (Fig. 3). Moreover, only two reaction rate intervals are observed with the maximum rate (R_{pmax}) occurring at conversions (X_{max}) around 20%. For the polymerization of VA in three-component microemulsions stabilized with the cationic surfactant, cetyltrimethylammonium bromide (CTAB), also two reaction rate intervals were reported with R_{pmax} occurring at X_{max} ca. 20%, regardless of monomer and initiator concentration [19]. According to a recent model for microemulsion polymerization [33,34], X_{max} is directly related to the volume fraction of monomer in the particle at equilibrium (ϕ) when the aqueous phase is saturated with monomer. Hence that X_{max} is the same in the absence or presence of *n*-BuOH implies that ϕ and the monomer saturation concentration in the aqueous phase are not modified by the presence of the alcohol. This result may be a consequence of the small amount of *n*-BuOH (0.485 wt%) employed and also suggests that most of the *n*-BuOH is located at the interface and/or the continuous aqueous phase [21].

Even though the polymerization kinetics for the alcohol-free and the AOT/*n*-BuOH systems follow almost identical paths (Fig. 3), the evolution of particle size (Fig. 4), number density of particles (Table 1), average molar masses (Fig. 5) and the MMD (Fig. 6) are quite different. How can one explain these results?

It has been reported that KPS decomposes more rapidly in aqueous solutions of alcohols [35]. If this were the case, faster reaction rates should be observed, contrary to experimental results. Also, it has been reported that VA affects the decomposition rate of KPS due to the existence

of an electron transfer mechanism [36,37]. However, in the polymerizations examined here, the overall concentrations of VA and KPS are identical and so, this effect should be the same for both systems.

In the microemulsion polymerization of a given monomer at the same temperature, k_p should be constant and so, reaction rate depends on: (i) monomer concentration in the active particles $[M]_p$, (ii) number density of particles, N_p , and (iii) average number of free radicals per particle, \bar{n} [8, 18,33,34]. Examination of each of these factors in the polymerization of VA in the AOT and AOT/*n*-BuOH microemulsions may explain the nearly identical reaction rates.

As discussed above, monomer concentration within the particles should be similar at all conversions inasmuch as the volume fraction of monomer at equilibrium within the particles seems not to be modified by the presence of *n*-BuOH and because overall monomer concentration (3 wt% in both formulations) is the same in both systems.

In the polymerization of VA in the alcohol-free microemulsion, particle size increases rather slowly up to 50% conversion and then more rapidly. For the polymerization in the microemulsion containing *n*-BuOH, particles grow continuously through all the reaction. Also, particles are larger throughout the reaction in the alcohol system than those in the alcohol-free system (Fig. 4). This is a consequence of the smaller overall concentration of AOT used in the alcohol system, which may facilitate particle coagulation, as discussed below.

Table 1 shows that N_p diminishes at relatively low conversions in the AOT/*n*-BuOH system and at higher conversions in the alcohol-free system, probably due to particle coagulation. The smaller number of particles in the AOT/*n*-BuOH system suggests that *n*-BuOH is not as good surfactant as AOT and leads to larger particle size. The occurrence of coagulation during the emulsion polymerization of polar monomers has been, in fact, reported elsewhere [38,39]. Moreover, it seems that the smaller AOT content in the alcohol system and the presence of the non-charged alcohol molecules at the interface weakens the electrostatic repulsion forces among the particles (decreasing the thickness of the Debye double layer) and facilitates particle coagulation. For the polymerization of styrene in microemulsions containing different short chain alcohols, an enhanced degree of coagulation was reported [40]. This effect was more severe when *n*-butanol was used as cosurfactant [40]. Since continuous particle nucleation is a characteristic of microemulsion polymerization, we suggest that the rate of coagulation overpowers the rate of nucleation in such a way that particle growth and an overall decrease in N_p are observed. Hence, since N_p is larger throughout the reaction in the alcohol-free system but the reaction rates are similar, this parameter cannot explain the similarity in reaction rates.

Another factor that contributes to particle growth is the radical desorption rate because it changes the average

number of free radicals per particle (\bar{n}). When the reacting particles are small, desorption rate is high and so the radicals formed by chain transfer to monomer have a low probability of initiating new chains inside the particles. However, as particles become larger due to the formation of new polymer chains by radical entrance or by coagulation, the probability for monomeric radical desorption drops and, as a consequence, particles grow as more polymer chains are formed inside the particles. Therefore, the escaping probability of a monomeric radical should diminish as particles grow. This should give as a result, an increase in the average number of radicals per particle. Hence, we suggest that \bar{n} is larger in the AOT/*n*-BuOH system because particles are larger. The combination of a lower number density of particles and a higher average number of free radicals per particle in the AOT/*n*-BuOH system may explain why the reaction rate is similar to that in the alcohol-free system, which has a larger number density of particles. Also, as discussed below, this hypothesis explains the differences in particle size and MMD.

As particle size increases, radicals should remain more time in the particles. Hence, the probability of chain transfer to polymer should increase giving as a result, branched polymers with higher weight-average molar masses [19]. Because of the larger particle size obtained in the system stabilized with AOT/*n*-BuOH (Fig. 4), it could be expected polymers with higher molar masses, compared to those produced in the alcohol-free system. However, the opposite trend is observed at all conversions (Fig. 5).

At low conversions, the MMD for the AOT/*n*-BuOH system is almost symmetric whereas that for the alcohol-free system has a small shoulder at the high molar mass side of the distribution (Fig. 6A). Elsewhere we showed that chain transfer reactions to monomer are the controlling mechanism for chain termination at all conversions in microemulsion polymerization [19,20], but chain transfer reactions to polymer may also occur even at low conversions. The latter mechanism is responsible for the appearance of the high-molar mass shoulder in the alcohol-free system. On the other hand, the absence of this shoulder in the AOT/*n*-BuOH system suggests that chain transfer reactions to alcohol contribute to the formation of shorter chains and to reduce chain transfer reactions to polymer due to the lower number density of high molecular weight species. This is supported by the fact that the MMD of the AOT/*n*-BuOH system is skewed toward the lower molar mass population (Fig. 6). However, as reaction proceeds, particles grow and a high molar mass population evolves in both systems. Hence, as particles grow, the probability that the radicals stay longer in the particles becomes higher. Also, as conversion increases, the concentration of macromolecules within the particles augments. The combination of these two factors leads to an increasing number of chain transfer reactions to polymer, which in turn, result in branched polymers with higher weight-average molar masses. Moreover, since coagulation

seems to be important, we propose that collision and coagulation of two active particles contribute to the high molar mass population.

Notice that at final conversions, a bimodal distribution has developed in both systems (Fig. 6B). To reconcile that particles are larger, M_w is smaller and the MMD's are skewed toward the lower molar mass population for the AOT/*n*-BuOH system, we propose that transfer reactions to alcohol molecules compete with transfer reactions to polymer, due to the high chain transfer constant of *n*-BuOH (20×10^{-4}) [41] to reduce the formation of high molar mass polymer, in spite of the large chain transfer to polymer constant of PVA ($C_P = k_{tr,P}/k_P = 1.2\text{--}8.0 \times 10^{-4}$) [41].

To show conclusively the chain transfer effect of *n*-BuOH on the microemulsion polymerization of VA, MMD's of PVA's were obtained at different molar ratios of *n*-BuOH/VA [43]. Fig. 7 displays a plot of the inverse of the degree of polymerization (X_n^{-1}) versus the molar ratio of *n*-butanol-to-VA, $[n\text{-BuOH}]/[VA]$. This plot shows that the inverse of the degree of polymerization increases almost linearly with increasing $[n\text{-BuOH}]/[VA]$, which is expected when a chain transfer agent is added to a reacting system [44]. The slope of this line should give the value of the chain transfer constant, C_{tr} , of the *n*-BuOH. The value obtained is 11×10^{-4} , which compares well with reported values [41]. Additionally, Sosa et al. [42] report that M_n of the PVA prepared without *n*-BuOH is about 129,500 Da which is greater than the values obtained with the different $[n\text{-BuOH}]/[VA]$ (67,000–84,500 Da).

5. Concluding remarks

We have shown that the addition of an alcohol cosurfactant enhances the o/w microemulsion region and allows, upon polymerization, the formation of poly(vinyl acetate) of lower average-molar mass than that obtained with emulsion and alcohol-free microemulsion polymerization using AOT as surfactant [42]. Polymer particles in the

resulting latexes, on the other hand, are larger in the AOT/*n*-BuOH system than those in the alcohol-free system, but smaller than those obtained in the AOT-stabilized emulsion polymerization case [42]. The smaller particle size of the microemulsion-made latexes (with and without alcohol) favors the exit of the monomeric radicals from the particles and hence, promotes lower molar masses than those obtained by emulsion polymerization of this monomer. Also, the presence of the alcohol, which is a chain transfer agent [41] and which decreases the electrostatic interactions at the droplet's (and particles') interfaces, allows faster entry and exit of radicals. This behavior leads to lower molar masses and narrower MMD. Finally, it is important to remark that neither solution nor emulsion polymerization can explain the results reported here. First, the molar masses obtained here are larger than those typically produced by solution polymerization of this monomer [32] but lower than those commonly reported by emulsion polymerization [25,26]; also, in the latter process, the extent of branching and gel are much higher. Second, the polymerization kinetics follows the classical microemulsion polymerization mechanism and differs from that of a batch emulsion polymerization of this monomer, i.e. no constant rate interval is observed and the maximum reaction rate is detected at much higher conversions [45].

The potential of microemulsion polymerization for making high-molar mass PVA without gel nor branched polymer with high conversions (100%) is enormous, specially in the light of the methods developed recently to increase the polymer content in these latexes without adding more surfactant [42,46–49].

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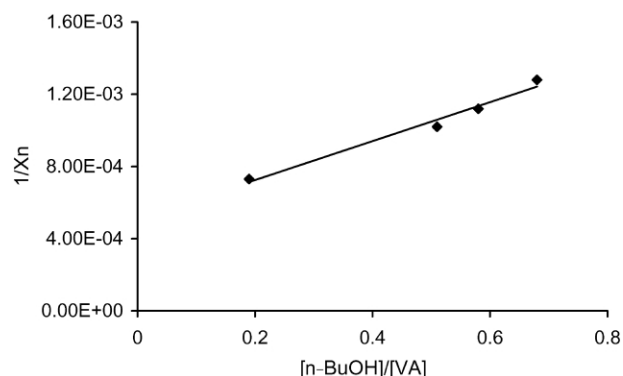


Fig. 7. Inverse of the average degree of polymerization versus the $[n\text{-BuOH}]/[VA]$ molar ratio for the microemulsion polymerization of VA at 60 °C initiated with 0.03 wt% KPS.

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