Surfactant Concentration Effects on the Aqueous Phase Polymerization of Vinyl Acetate

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Summary: Vinyl acetate (VAc) in concentrations below the water saturation value was polymerized by batch processes at 60 °C using low surfactant concentrations of sodium dodecyl sulfate (SDS) and potassium persulfate (KPS) as initiator. The effects of surfactant concentration on the reaction kinetics, particle formation and molecular weight were studied. It was found that the average particle diameters decrease between 277 and 18.7 nm as the surfactant concentration is increased from 0 to 11 mmol/L, whereas the weight average molecular weight (Mw) decreases also, with values between $8.7 \times 10^5 \leq Mw \leq 1 \times 10^5$ Da. It was observed that particle size distributions are strongly affected by the addition of small amounts of surfactant. For the low monomer concentrations used in the polymerizations (0.0137 g/cm^3 of water), particles were very stable and no coagulation was observed. High reaction rates were found in all polymerizations. When no SDS was added to the system, lower polymerization rates were obtained at the onset of the reaction due to the low rate of particle formation. The behavior of polymerization rate was inversely proportional to the surfactant concentration, which was ascribed to the increase in the average number of radicals per particle.

Keywords: aqueous phase polymerization; emulsion; latex; vinyl-acetate

Introduction

Monomers like vinyl acetate with relatively high water solubility can be polymerized in absence of any added surfactants using a water soluble ionic initiator such as potassium persulfate.[1] Stabilization of latex polymer particles can be possible due to the in situ surfactant formation of the oligomers formed in the aqueous phase which contain a charged hydrophilic group derived from the initiator. These amphiphilic oligomers operate as surfactants with the charged head directed to the aqueous phase whereas the organic part is oriented to the core of the polymer particle. Until now, some work has been made intended to elucidate the mechanism of particle formation in the aqueous polymerization of vinyl acetate.[2–5] For example, Dunn and Taylor[3] studied the effects of the reaction conditions on the polymerization rate and on the number of particles when KPS is used in the aqueous polymerization of VAc. They concluded that the surface charge density is the factor which determines the number of particles formed and which limits the rate of reaction. They indicated that beyond the particle nucleation period, most of the polymerization takes place in the latex particles. This is presently the generally accepted reaction locus.[4] While the aqueous phase is not an important locus of polymerization with respect to the relative quantities of monomer converted

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to polymer, the species formed in this phase are of importance because of their influence on the number of particles formed through the reaction (homogeneous – coagulative nucleation). Thus, in surfactant free polymerizations, the number of particles would be proportional to the number of chains initiated in solution (which grow to the critical size and then precipitate) with a possible reduction in this number due to radical combinations or capture by a particle before homogeneous particle formation occurs and to coagulative nucleation. In classical emulsion polymerization, the final particle number is the total number of primary particles minus the number of particles coalesced during the course of reaction.[2]

Although particle formation in aqueous phase polymerization of VAc has been reported, few efforts have been made to explain the molecular weight behavior when VAc is polymerized in aqueous solution and when low surfactant concentrations are used. The present work reports the VAc polymerization using surfactant concentrations below and above the critical micellar concentration (CMC) and VAc concentrations below the saturation value in water. The aims of this research were to investigate the mechanisms of particle formation during VAc polymerization in aqueous continuous phase as well as to investigate molar masses development. For practical purposes, the results could be useful to elucidate these phenomena in VAc polymerization processes in which water is the continuous phase (such as aqueous phase polymerization, emulsion and microemulsion polymerizations).

Experimental Part

Tri-distilled grade water was employed. Tetrahydrofurane (THF) used as mobile phase for molar mass determinations was HPLC-grade. All reactants (purity $\geq 99\%$) were purchased from Aldrich. VAc was distilled under reduced pressure, kept under refrigeration, protected against light

and used within a week. SDS and potassium persulfate (KPS) were used as received. The CMC of SDS in water was measured by conductimetry in presence of vinyl acetate ($0.0137\,g/cm^3$ of water) and potassium sulfate ($8.8 \times 10^{-5}\,g/cm^3$ of water) at $60\,°C$; the concentration of the VAc was the same as that used in the reaction mixtures and that of potassium sulfate was the molar equivalent to that of the potassium persulfate used as initiator.

The polymerizations were carried out in duplicate at atmospheric pressure and $60\,°C$ in a $1\,L$ glass jacketed reactor with three inlets equipped with a reflux condenser. The compositions of polymerized mixtures are given in Table 1. The reaction mixture was stirred mechanically at $330\,rpm$. At the beginning, water, SDS and KPS ($2\,wt.$-% with respect to the VAc) were charged to the reactor; the solution temperature was increased to $60\,°C$ and then argon of ultrahigh purity was bubbled for an hour to eliminate oxygen. Then, the batch polymerization was started with a one-shot addition of oxygen-free VAc. The stream of argon was maintained into the reaction mixture during the whole polymerization process.

Samples were taken at specific times, the reaction stopped with $0.5\,mL$ of 0.01% hydroquinone solution and freeze dried for conversion determination by gravimetry. Particle size was determined by quasi-elastic light scattering with a Nano S90 (Malvern) apparatus at $25\,°C$. The latexes were diluted as necessary with tridistilled and filtered ($0.2\,\mu m$ pore size) water before the measurements. The calculation of Np was carried out with equation (1).[6] Where $[M]_0$ is the initial monomer concentration in the reactor, X is the conversion, Dp_v is the experimental volume-average diameter

Table 1.
Formulations used in polymerizations.

Run	VAc (g)	SDS (g)	KPS (g)	Water (g)
A	14.20	0.0	0.30	1035.0
B	14.20	0.766 (2.57 mmol/L)	0.30	1035.0
C	14.20	1.530 (5.13 mmol/L)	0.30	1035.0
D	14.20	3.30 (11.0 mmol/L)	0.30	1035.0

of the particles and ρ_p is the density of the polymer. In equation 1, we have used z-average diameter obtained from light dispersion.

$$N_p = \frac{6[M]_0 X}{\pi D p_v^3 \rho_p} \tag{1}$$

To eliminate surfactant from the polymers, the obtained samples were washed several times with hot water and then freeze dried for molar mass determinations. Average molar masses of polymers (previously dissolved in THF) were determined in a Hewlett-Packard series 1100 gel permeation chromatograph apparatus equipped with a refractive index detector and three PL Gel serial columns (Pore sizes 103, 105 and 106 Å). The GPC was calibrated with narrow polystyrene standards (Polymer Laboratories) using Mark – Houwink parameters for polyvinyl acetate (PVAc) taken from the literature ($\alpha = 0.708$ and $K = 15.6 \times 10^{-3}$).[7]

Results and Discussion

Critical Micelle Concentration

There are reports indicating that the CMC of SDS can be affected by the presence of some monomers when their concentration in water is below the saturation value. Therefore, the CMC of SDS in water and in the presence of VAc and potassium sulfate was measured in order to determine if there is a relationship between the sizes of the polymer particles with the initiation of the polymerization in the micelles when SDS is used. In order to avoid polymerization during the CMC determination at 60 °C, KPS was replaced with the equivalent moles of potassium sulfate. The CMC of the system employed was found to be 7.7 mmol/L, which agrees with values previously reported at similar conditions[2] and below to that reported in pure water.[8] Donescu et al.[9] found that hydrophobic monomers are solubilized toward the hydrocarbon interior of the micelles whereas the hydrophilic ones, toward the polar head of the surfactant, this localization of the hydrophilic monomers (water solubility of VAc ≈ 2.5 g/100 g of water[10]) have a synergistic effect as a co-emulsifier by introducing enough separation between the sulfate groups. However, it has been reported that the CMC of surfactants in the presence of water soluble monomers does not change upon further addition of monomer beyond its saturation value.[2]

Kinetics and Particle Formation

Initially, clear reaction mixtures turned bluish and translucent at the early stages of the reaction, and became less translucent towards the end of the polymerization, except when no surfactant was used in the recipes, in that case, opaque latex was obtained as can be seen in Figure 1. The latexes were very stable and no phase separation or precipitation was observed after two months of storage.

Figure 2(a) shows conversion vs. time as a function of surfactant concentration. High final conversions were obtained, except for
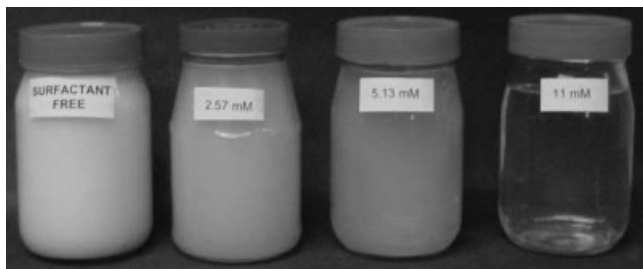

Figure 1.
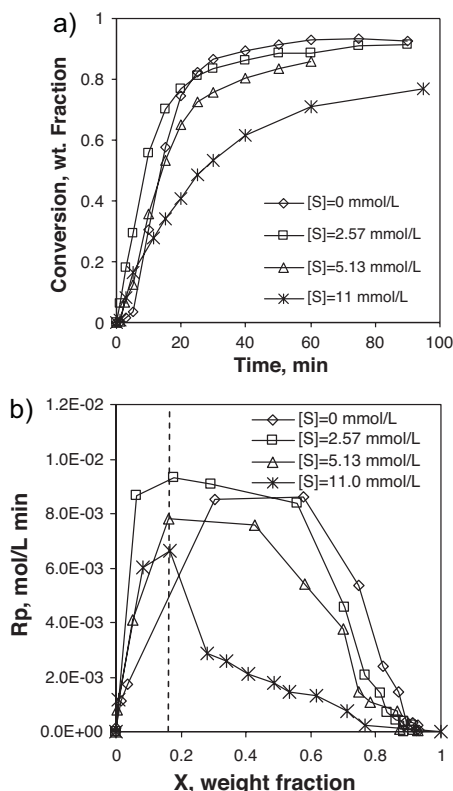Aspect of the final latexes obtained from polymerisations.

Figure 2.

(a) Conversion vs. time and (b) Polymerization rate vs. conversion of batch aqueous polymerization of vinyl acetate at 60 °C for different surfactant concentrations.

CMC. For surfactant concentrations below the CMC, there are not micelles and the particles are formed by the contribution of surfactant, surface active oligomers derived from initiator and the VAc present in the reaction medium, which acts as co-surfactant. When no SDS is added, particles are formed only due to the surface active oligomers and the VAc.

As can be seen in Figure 2b, the polymerization rate decreases as the surfactant concentration is increased and Rp_{max} occurs at ∼16% (dashed line) conversion independently of the surfactant concentration employed, except when no surfactant is used (Rp_{max} occurs at ∼30% conversion). In emulsion polymerization Rp is given by

$$R_p = \frac{k_p [M]_p N_p \tilde{n}}{N_A} \qquad (2)$$

where k_p is the propagation rate constant, $[M]_p$ is the volume fraction of monomer within the particles, $\tilde{n}$ is the average number of radicals per particle and N_A is Avogadro's number. Assuming that equation (2) is valid for the reactions reported here, and taking into account that the initial monomer content is the same, which implies that at a given conversion $[M]_p$ is the same in all the reactions, independently of the surfactant concentration employed, then, either $\tilde{n}$ or N_p should cause the dependence of reaction rates with [SDS].

Figure 3 shows the maximum polymerization rate (Rp_{max}) and the weight average molecular weight (Mw) of the final polymers as a function of the SDS concentration. It can be seen (curve 1) that Rp_{max} decreases by increasing the surfactant concentration. The reaction order with respect to SDS concentration was −0.23. Similar behavior has been reported by Donescu et al.[12] for the VAc polymerization with SDS and n-propanol as surfactant and co-surfactant, respectively. They found an order of −0.5 for reactions where the SDS concentration was several times the CMC. Donescu et al. attributed this behavior to strong transfer of the growing radical to SDS to generate low reactivity radicals that decrease the reaction rate.
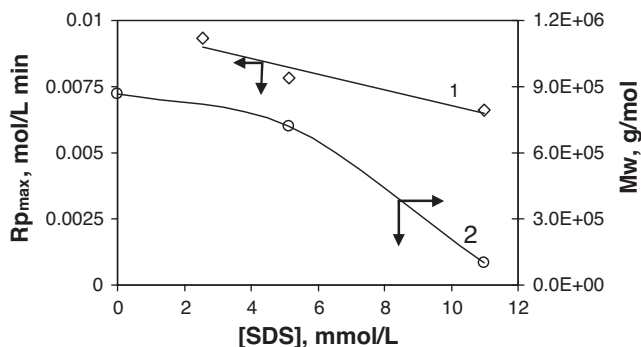
the reaction where the surfactant concentration was 11 mmol/L. Figure 2(b) shows the polymerization rates as a function of conversion, where it can be seen that when the surfactant concentration used is above the CMC (11 mmol/L) two polymerization periods are observed, which is typical of microemulsion polymerization where particle formation throughout the reaction has been reported.[11] The first period corresponds to polymer particle formation and growth until the maximum in Rp is reached around 16% of total conversion; then, Rp starts to decrease because the monomer in the particles is being depleted. Nevertheless, the three classical emulsion polymerization rate periods are observed when the surfactant concentration used is below the

Figure 3.
Maximum polymerization rate and Mw vs. SDS concentration observed in the batch aqueous polymerization of vinyl acetate at 60 °C.

However, this is open to discussion because when alcohols are used as co-surfactants, chain – transfer to alcohol molecules events are strong in the polymer particles.[13] Besides, alcohol – transferred radicals favor the water-phase termination events or decreases the average degree of polymerization of oligomeric radicals (suppresses homogeneous nucleation).[14] In our work, the molar masses of the final polymers decrease with the increase of SDS concentration (Figure 3, curve 2). As will be discussed below, this behavior of molecular weight with surfactant concentration is related to desorption of monomeric radicals from the polymer particles to the aqueous phase.

Figure 4 shows the evolution of average particle size as a function of conversion for different surfactant concentrations. Particle size increases with increasing conversion but decrease as surfactant concentration is increased in the formulation. Particle size distributions (PSD) obtained by QLS of resulting latexes from VAc polymerizations at different conversions using different surfactant concentrations are shown in Figure 5. Broad PSDs which are shifted to higher diameters as conversion increases were obtained when the surfactant concentration is below the CMC.

When the surfactant concentration is above the CMC, the broadening of PSD as polymerization proceeds is less evident. As shown in Figure 6, a small increase in the

surfactant used (from 0 to 2.57 mmol/L) has a significant effect on the width and average particle diameter of the PSD of the latexes. It is worth mentioning that after 14 month of storage, the latexes where surfactant was used became transparent because of hydrolysis of PVAc to yield polyvinyl alcohol, PVOH. However, the latex obtained in surfactant – free polymerization remains unchanged (the Dp remained almost constant at 274 nm). It has been reported that the rate of hydrolysis is slightly higher for the low molecular weight than for the high-molecular weight PVAc.[15] However, more
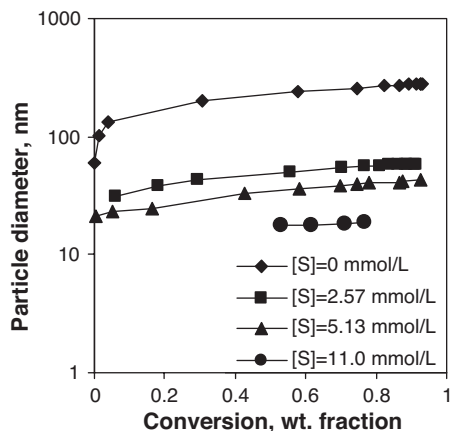

Figure 4.
Average polymer particle diameter vs. conversion of batch aqueous polymerization of vinyl acetate at 60 °C for different surfactant concentration obtained by light dispersion.
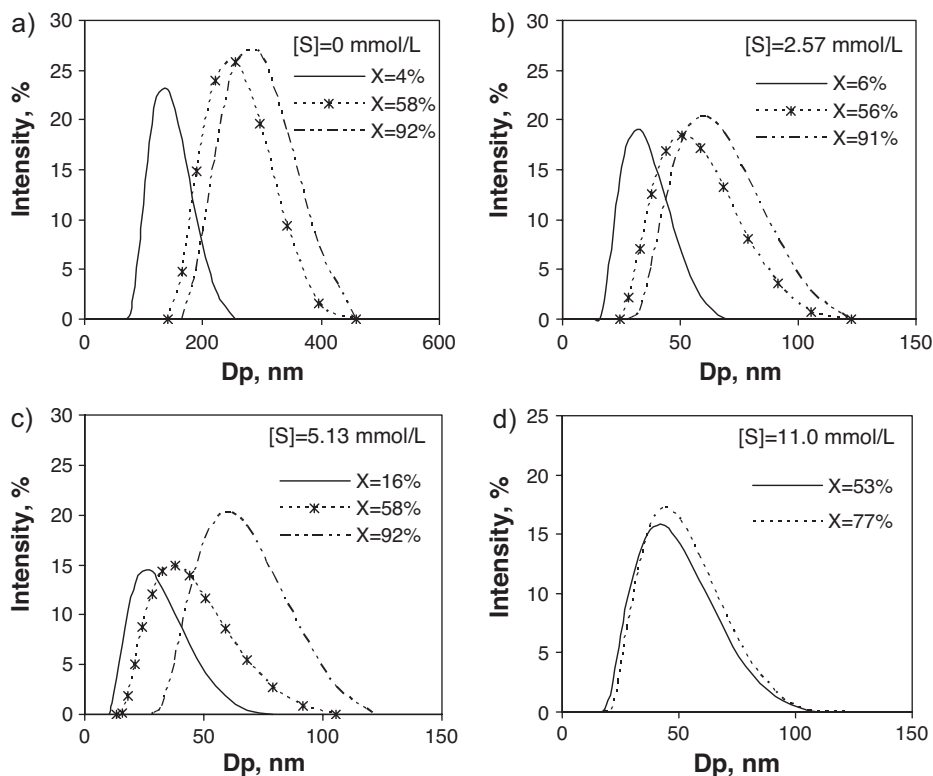
Figure 5.

Particle size distribution of the latexes obtained at different conversions and surfactant concentrations.

work is needed to explain the effect observed in this research.

In the polymerization of monomers with low water solubility such as styrene and butyl methacrylate using surfactant concentrations above the CMC (microemulsion systems), Dp increases at the beginning of reaction and then it remains roughly
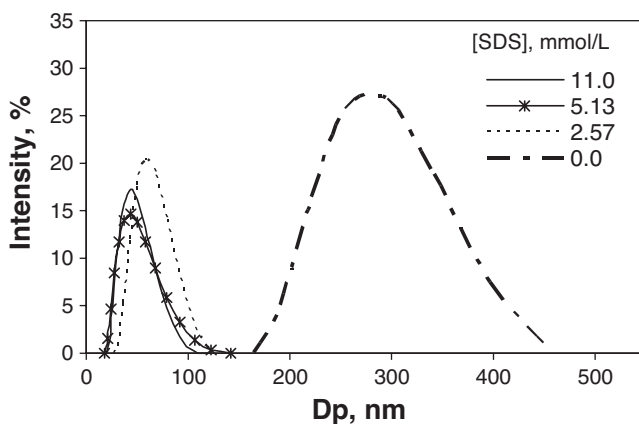

Figure 6.

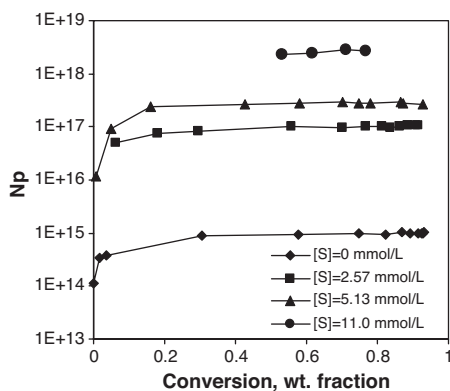PSDs of the final latex obtained using different surfactant concentrations.

Figure 7.

Polymer particle number vs. conversion for batch aqueous polymerization of vinyl acetate at 60 °C for different surfactant concentrations.

constant throughout the reaction.[16,17] In Figure 7, an increase in Np with conversion and surfactant concentration can be observed.

It is well known that the average particle size, at any time in the polymerization, is influenced principally by three factors: the growing of the existing particles by monomer conversion inside them, particle coagulation and, continuous formation of new polymer particles. Monomer conversion and particle coagulation cause an increase in the average particle size, of which, particle coagulation causes a suddenincrease in the average diameter. On the other hand, depending on their complex interrelation with the factors mentioned before, the formation of new particles can reduce or maintain the average Dp.

In our case, the large increase in particle size with conversion may be due, in minor part, to particle coagulation, because based on Figure 7, in any case the number of particles does not decrease as the reaction proceeds, so we can ignore particle coagulation and state that the increase in the average particle size is mainly due to the growing of the existing particles by monomer conversion.

It is generally accepted that in free radical polymerizations in which only the monomer and ionic initiator are present in the water phase, the mechanism of particle formation is by coagulative nucleation.[18,19] We need to make clear that this coagulation process is treated purely as a mechanism of particle formation but has not relation with coagulation of mature polymer particles.

In Figure 4, we can see that there is a clear dependence between the surfactant concentration and the average particle size. When surfactant below its CMC is used, the mechanism of particle formation is very similar to the coagulative nucleation,[20] but in this case, due to surface active properties of the surfactant molecules, the colloidal stability of the precursor particles is reached faster and then the extension of the coagulative process must be reduced, reducing the final size of the new polymer particles formed with respect to that attained in surfactant – free polymerization and this effect is directly proportional to surfactant concentration in the water phase. Above the CMC ([SDS] = 11 mmol/L) the average particle size is typical of those reported by microemulsion polymerization of VAc.[11,21] Micellar nucleation is the most important mechanism of particle formation in this type of polymerization and although there is high surfactant concentration it is considered that coagulative nucleation does not compete with micellar nucleation because of the high interfacial area of the polymer particles and the monomer droplets, which capture most of the oligomeric radicals formed in the aqueous phase.

From Figure 7 we can see that the curves for the number of particles exhibit dependence on surfactant concentration too. If we accept that the surfactant molecules help to the precursor particles to reduce the extension of the coagulative process, stable particles form faster and the rate of particle formation increases, so, at the same conversion highest number of particles are formed as surfactant concentration increase. On these bases, the strong dependence of Np on surfactant concentration below the CMC can be explained. On the other hand, it can be stated that coagulative

nucleation must be a very fast process because high Np is reached at the start of the polymerization with diameters of considerable size.

Aditionally, in Figure 7, it is noticeable that for the polymerizations of 0, 2.57 and 5.13 mmol/L of SDS, the bulk of Np is formed at conversions between zero and the one corresponding to the maximum rate of polymerization (Figure 2b). After this conversion, it appears that the formation of particles practically stops. This could be attributed to depletion of the surfactant and monomer concentration in the water phase; however, Figure 8a shows that in all the polymerizations carried out, over the entire range of conversion, there is an excess of surfactant dissolved in the water phase (although surfactant concentration in the formulation is low, the interfacial area of the polymer particles is too high and

consequently the surfactant employed is enough to cover the particle surface at 100% and the excess is dissolved in the water phase). The drop in monomer concentration in the water phase can not be the cause of the end of particle formation because it was found that its concentration falls linearly with conversion until the end of polymerization and its concentration at the point where particle formation stops is still considerable. A major factor, at which this phenomenon can be attributed, is the increase of the surface area of the polymer particles. An interesting correlation appears when the number of particles is compared with the corresponding interfacial area of the polymer particles.

Figure 8(b) suggests that there is a surface area of polymer particles (dashed line), for each surfactant concentration below CMC, at which the velocity of particle formation decreases. The change in this velocity could be explained because at this point, the probability of capture of aqueous phase oligomers by polymer particles becomes more important, and then, reduces the quantity of oligomers that reaches the critical size length and as a result reduces the formation of precursor particles too. It was found that this change corresponds to the maximum rate of polymerization observed at conversions of 30% and 16% respectively for the polymerization of 0, 2.57 and 5.13 mmol/L of SDS. Thus, we can think that, at a particular initiator concentration, the surface area and the number of particles are the factors that determine the extension of the period of particle formation and consequently, the conversion at which the maximum rate of polymerization is reached. On the other hand, the surfactant concentration determines the velocity of particle formation and therefore the maximum polymerization rate.
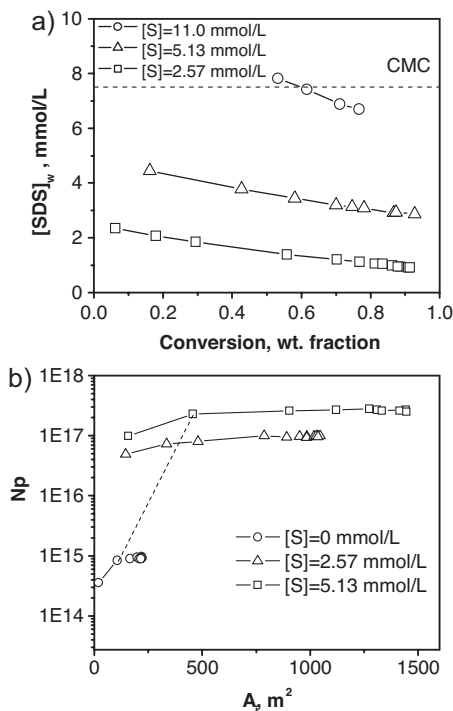

Figure 8.

(a) Surfactant concentrations in the water phase vs. conversion and (b) Particle number vs. interfacial area of polymer particles, at different surfactant concentrations used in the formulations.

Molar Mass

As can be seen in Figure 3, the weight average molar masses decrease as [SDS] increases. In Figure 9, the molar mass distributions (MMD) of the polymers
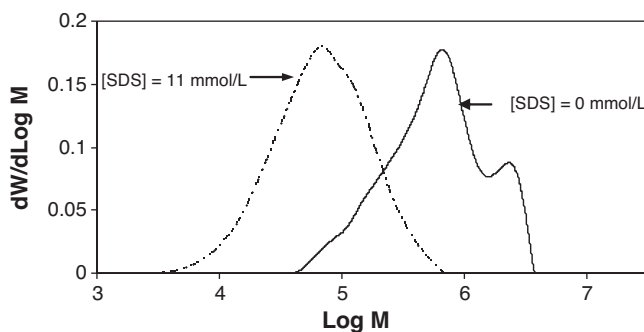
Figure 9.
Molar mass distributions of the polymer corresponding to [SDS] = 0.0 and 11 mmol/L obtained at the end of reactions.

corresponding to the higher and the lower [SDS] (11 and 0 mmol/L) obtained at the end of the reactions, are shown. It is clear that when no surfactant is used, a shoulder at high molar masses is obtained, which is less noticeable by increasing the surfactant concentration. For this process, the reaction rate, Rp, is given by equation 2.

Because all reactions reported here were made at the same temperature and with the same monomer, k_p must be the same. Also, the initial monomer content is identical in all reactions, hence the value of $[M]_p$ depends only on conversion; as a result, at a given conversion, $[M]_p$ is the same in all the reactions, independently of the [SDS] used; for this reason, reaction rate depends on Np and $\bar{n}$. The average number of radicals per particle depends on the rates of radicals entering and exiting the particles. The probability of radical desorption from a particle, depends on the characteristic diffusion time of a monomeric radical on the length scale of the particle size and the

time scale of propagation, which means that the probability of radical desorption diminishes as the particle becomes bigger.[21] Under these circumstances, the average number of radicals per particle wascalculated from equation 2. Table 2 shows the average number of radicals per particle obtained at different conversions using different surfactant concentration. The value of $[M]_P$ was estimated assuming that the monomer volume fraction (ϕ) within the particles decreases linearly with conversion from its saturation value[22] ($\phi_s = 0.85$[23]) at the beginning of the polymerization as, $\phi/\phi_s = 1 - X$. Then $[M]_P$ can be estimated from $[M]_P = \phi \rho_m / M_0$, where ρ_m and M0 are the density (820 g/L at 60 °C[24]) and the molar mass of the monomer, respectively.

The high values of $\bar{n}$ when [SDS] = 0.0 are normally observed when all radicals produced in the aqueous phase are captured by the polymer particles, no radicals diffuse out, and particles are big enough to

Table 2.
Average number of radicals per particles (ñ) obtained at different conversions as a function of surfactant concentration.

[SDS] = 0.0 mmol/L		[SDS] = 2.57 mmol /L		[SDS] = 5.13 mmol /L		[SDS] = 11.0 mmol /L	
X	ñ	X	ñ	X	ñ	X	ñ
0.037	0.718	0 .179	0.023	0.050	0.0068	0.532	0.0002
0.577	3.240	0.558	0.027	0.427	0.0072	0.616	0.0002
0.822	2.073	0.768	0.013	0.700	0.0064	0.711	0.0001
0.892	0.533	0.862	0.005	0.874	0.0005	0.767	0.0001
0.932	0.078	0.914	0.001	0.927	0.0064		

contain more than one radical at the same time. In contrast, the low values of $\tilde{n}$ indicate that radicals can diffuse out of the particles quite readily, which is reasonable for radicals of low molecular weight. Moreover, a quick analysis of the minimum particle diameter from which a monomeric radical reacts with another monomer molecule rather than escaping from the particle can be estimated with Einstein's diffusion equation. For two values of the diffusion coefficient, 10^{-6} and 10^{-7} cm^2/s,[5] values of Dp = 190 and 60 nm, respectively, were obtained as the limits of particle size from which a monomeric radical can escape rather than reacting there. In our results, when no surfactant was used, particle diameters between 59 and 270 nm were observed throughout the reaction. For this reason, the probability that various radicals coexist within a particle increases for this particle size range. When the poly (vinyl acetate) is obtained by aqueous polymerization without added surfactant, particles are bigger and the number of chains per particle (N_C) is also much larger and so, chain transfer to polymer is more viable giving as a result larger molar masses.

The shoulder of high molar mass population for [SDS] = 0 in Figure 9 is explained because the radicals into the polymer particles stay longer time increasing the probability of chain transfer to polymer. However, when the surfactant concentration is increased, chain transfer to monomer and radical desorption become important.

Conclusions

The findings reported in this work could be useful to explain the development of PSD and molar masses in the aqueous phase polymerization of vinyl acetate. Under the conditions studied a small presence of SDS has a dramatic influence on Dp and PSD: Dp decreases and the PSD narrows falling in the range reported for microemulsion polymerizations. The molar masses of the final polymers decrease with the increase of [SDS]: this behavior of molecular weight with surfactant concentration is related to desorption of monomeric radicals from the polymer particles to the aqueous phase.

When vinyl acetate solubilized in water is polymerized, particles are bigger and the number of chains per particle is much larger and chain transfer to polymer is more viable giving larger molar masses. However, when [SDS] is increased, chain transfer to monomer and radical desorption become important producing poly (vinyl acetate) of lower molar masses.

The high surface area of the particles prevented the occurrence of coagulation. In our case, the stability of the system against coagulation was preserved during the whole course of the polymerization although hydrolysis was found after 14 months of storage in the latexes prepared with SDS. The surfactant-free latex did not hydrolyze.

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