TEMPERATURE INFLUENCE ON SURFACTANTS ADSORPTION ONTO POLY(VINYL ACETATE) LATICES PREPARED VIA SURFACTANT-FREE EMULSION POLYMERIZATION

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Poly(vinyl acetate), PVAc, latices have been prepared via surfactant-free emulsion polymerization using potassium persulfate (KPS) as initiator. Both the conversion and the particle size increase with concentration of KPS. Transmission electron microscopy measurements show a narrow particle size distribution, which makes such latices useful for studying surfactant adsorption. The adsorption of sodium dodecyl sulfate and Brij 56 (a nonionic polyethoxylated surfactant) onto PVAc latex particles has been investigated using steady-state fluorescence to assess the ratio between free and adsorbed surfactants molecules, their critical micelle concentrations (*cmc*) and the adsorption surface area per surfactant molecule (a_s) at various temperatures (23-70^{0}C). A significant effect of temperature on I_1/I_3 ratio of pyrene, *cmc* and a_s is observed.

INTRODUCTION

In the past few decades, particles with high uniformity have found widespread applications in both academic and practical field.[1-8] Latices having a narrow particle size distribution can be obtained by surfactant-free emulsion polymerization (SFEP), a technique by which a monomer with low water solubility is polymerized in the presence of a water-soluble initiator. As a result, all charged groups are covalently linked to the polymer chain and the particles electrostatically stabilized, having a rather low charge density. The radicals grow up to a critical chain length and generate particles after the separation from aqueous phase. These particles are unstable and coagulate to form stable primary particles.[9]

The size of the latex particles obtained following the route of SFEP is normally ranged between 100 and 500 nm, giving a large specific surface area. Such a feature makes these uniform particle dispersions ideal for the adsorption studies. Many data are available for different surfactants (ionic and nonionic) especially onto polystyrene latices,[10-13] but not only.[14,15] The importance of this phenomenon is vital in emulsion polymerization

and many other industrial applications. Indeed, besides their role in stabilizing the initial emulsion of monomer and the final latex, the surfactants control the rate of polymerization, influencing to a great extent the particle nucleation and particle size distribution. Furthermore, the colloidal and rheological properties of the polymer latices depend on surfactants adsorption onto polymer surface.

Both surfactant self-association and surfactant adsorption onto polymer surfaces are temperature-sensitivity phenomena to a less or more extent mainly depending on the nature of surfactant and the hydrophobic character of the adsorbent surface. Thus, critical micelle concentration (*cmc*) of ionic surfactants generally varies in a non-monotonic way over a large temperature range beyond which there is a monotonic increase in *cmc* with increasing temperature, whereas nonionic surfactants exhibit a significant decrease in *cmc* as a function of temperature.[16] On the other hand, the adsorption of ionic surfactants onto polymer latices is enhanced by temperature increasing,[17] contrary to that of nonionic surfactants which diminishes with temperature.[15] In spite of these relatively well-defined tendencies, it is difficult to predict surfactant behavior during adsorption processes at elevated temperatures (i.e. polymerization temperatures).

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The methods for determining the surfactant adsorption in disperse systems rely on the monitoring the equilibrium concentration of free surfactant in the aqueous phase, which can be accomplished by ion-selective electrodes, UV/VIS spectroscopy, refractive index, titration,[10,18] chromatography[19] or, more often, by surface tension measurements.[15]

In this study we focused on the investigation of surfactant-free emulsion polymerization of vinyl acetate (VAc) using different amount of potassium persulfate (KPS) as initiator. The self-assembly and adsorption of an anionic (sodium dodecyl sulfate, SDS) and a nonionic polyethoxylated surfactant (Brij 56) onto prepared polymer particles were studied by fluorescence probes.

EXPERIMENTAL

Materials. VAc (supplied by Merck-Schuchardt, with purity higher than 99%) was used as monomer and freshly distilled before use. KPS (99+%, Sigma-Aldrich Chemie GmbH), was used as initiator without further purification. SDS (≥99%, Fluka Chemie GmbH), Brij 56 (Sigma-Aldrich Chemie GmbH) and pyrene, Py, (p.a. for fluorescence, Fluka Chemie GmbH) were also used as received.

Latex preparation and characterization. Monodisperse poly(vinyl acetate) latices (PVAc) were prepared via batch surfactant-free emulsion polymerization at 70^0C. The reactions were carried out in a 250 mL, four-necked glass reactor equipped with stirrer, condenser, argon inlet and thermometer. A water jacket was used for temperature control. First, the monomer and water were added into reactor, while the solution of KPS was dropped when the system reached the polymerization temperature, with a flow rate of about 0.3 mL/min. The concentration of KPS was 0.6, 1.0 and 1.4 wt. %, respectively, with respect to the amount of monomer.

After polymerization starts, samples of approximately 1-2 mL were withdrawn from the reaction mixture at different time intervals for conversion measurements. The solid content and overall conversion were determined gravimetrically from the dried samples weights based on the total amount of monomer used.

The amount of sediment was evaluated using a Heinz-Janetzki centrifuge with a rotor diameter of 140 mm. Samples of latex with approximately 5 wt. % solid content were centrifuged for 30 min at 5000 rpm. After centrifugation, the supernatant was discarded and the samples were dried in an oven at 120^0C as long as constant weight was achieved. The percentage sediment content was calculated as the ratio between the weight of dried sediment and the corresponding weight of latex.

The average particle diameter, d_p, was obtained from transmission electron microscopy measurements employing a JEOL TEMSCAN 200 CX electron microscope at an acceleration voltage of 200 kV. The samples were diluted with distilled water (thousands of times) and then placed onto copper grids (3 mm in diameter) with a carbon-coated collodion film. After carefully blotting with a piece of filter paper on the border of the grid, the wet sample was allowed to air-dry at least several hours. The value for d_p was calculated by taking into account more than 200 particles.

Fluorescence measurements. A proper amount of Py solution (~10^{-5}-10^{-4} M in ethanol) was introduced in a volumetric flask (1L) and carefully spread over the flask wall. Then, the solvent was evaporated under a stream of air. Distilled and purified water was added and the fluorescence probe solubilized by vortexing for a couple of days at room temperature. The amount of initial stock solution of Py in ethanol and the volumetric flask were chosen so the final concentration of Py was cca 10^{-7} M. The latter solution was used as solvent for preparing the surfactants solutions utilized in this investigation and for diluting the obtained PVAc latices. All fluorescence measurements were recorded on a Jasco FP-6300 spectrofluorimeter.

Adsorption of surfactants onto PVAc particles. Prior to adsorption studies, the latices were cleaned by dialysis in order to remove traces of monomer, initiator or soluble oligomeric species. The samples were placed in dialysis tubes and left in distilled water (which was changed every several hours) until the water conductivity vary no more.

Samples of about 4 wt.% polymer were prepared by dilution of the dialyzed latices with an aqueous Py solution of 10^{-7} M followed by the addition of a proper amount of surfactant solution to obtain a surfactant concentration in aqueous phase well above its *cmc*, even after the saturated adsorption was reached. To achieve the equilibrium of saturated surfactant adsorption onto polymer particles, the system was let under gentle stirring for 24 hours. Then, 100 mL of latex were placed in a serum replacement cell, type UHP-43 from Advantec, with a polyvinylidene fluoride membrane (pore size 100 nm; Millipore) and sieved out at constant temperature. A sample of serum was withdrawn and diluted with aqueous solution of pyrene until I_1/I_3 ratio of Py falls into the range of I_1/I_3 values which borders an etalon curves (I_1/I_3 as a function of the surfactant concentration) in order to find the aqueous concentration of surfactant after its adsorption onto latex particles. Knowing the amount of surfactant adsorbed and the average particle diameter, the area occupied by a molecule of surfactant in the saturated adsorbed layer, a_s, can be calculated as follows:

$$a_s = \frac{6V_p}{N_A d_p [surf]_{ads}} \cdot 10^{14} \ (\text{in nm}^2) \qquad (1)$$

where V_p is the volume (in cm^3) of polymer in 1 L of dispersion, N_A is the Avogadro's number, d_p is the average particle diameter (in cm), and $[surf]_{ads}$ is the concentration of adsorbed surfactant (in mole/L).

RESULTS AND DISCUSSION

The effect of KPS concentration

In classical emulsion polymerization, when the initiator is added in the emulsion of monomer in water, the reaction can start both in aqueous phase (homogeneous nucleation) or in surfactant micelles (micellar nucleation) or even in monomer droplets (droplets nucleation). Statistically, all these types

of nucleation can occur simultaneously, but the reaction conditions can be chosen so that one mechanism is preponderant above the others. In the absence of surfactant, a water soluble initiator will start the reaction in homogeneous phase, leading to formation of growing surface active oligomers that subsequently become particles by precipitation or micelles by self-assembling.[1] Once the micelles are formed, the micellar nucleation will play a significant role in the next stages of the reaction.

The concentration effect of initiator on the rate of polymerization can be observed in Fig. 1, while the main characteristics of the prepared latices are listed in Table 1. Due to a water solubility of 2.40 wt.% for VAc[20], the reactions start almost immediately after the addition of KPS, the nucleation mechanism being homogeneous, at least in the first stage of the reaction. In the particular case presented here, as the concentration of initiator increases, the rate of polymerization increases, maximum conversion being obtained for latex L3 (approximately 90%) prepared with the highest concentration of KPS.

The shape of conversion versus time curves is a typical sigmoid with a concave upward and a level off between 80 and 90%. By graphically differentiation of conversion curves with respect to time, the maximum rates of polymerization, R_{pmax}, can be obtained. The values for R_{pmax}, listed in Table 1, indicate that the increase of concentration of KPS from 0.6 to 1 wt. % increases the rate of polymerization with approximately 6%, while passing from 1 to 1.4 wt. % KPS, the rate of polymerization rises with about 48%. It is important to notice that a large amount of initiator may induce both a high rate of initiation and termination, which negatively affects the engendering of the oligomeric species responsible for micelle formation. The fact that the increase of concentration of KPS does not negatively affect the maximum conversion and the rate of polymerization could be a proof that the nucleation mechanism is entirely homogeneous, but further investigations are required to clarify this aspect.
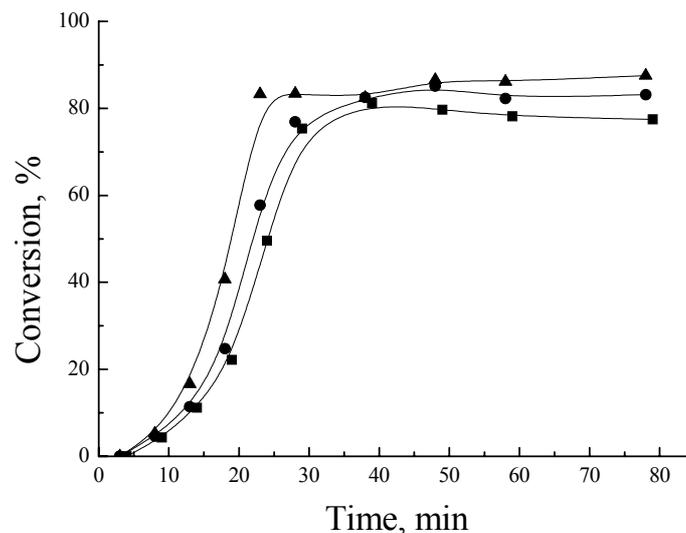

Fig. 1 – Plot of conversion vs time for polymerization of VAc with:
0.6 (■), 1.0 (●) and 1.4 (▲) wt.% KPS with respect to monomer weight.

Table 1

Characteristics of the PVAc latices

Characteristics	L1	L2	L3
Solid content, %	7.50	8.12	8.65
Sediment, %	2.97	3.11	3.29
$R_{p\ max}$ x 10^3, mole/Ls	1.25	1.33	1.97
d_p, nm	265	300	360

TEM images of the prepared latices can be seen in Figs. 2-4. All the latices have a narrow particle size distribution, the particle size increasing with concentration of initiator. Even though the increase of the concentration of the initiator gives rise to a larger number of ionic groups, and consequently, a

lot of particles area could be stabilized by the ionic oligomeric species, the increased ionic strength of the systems compresses the electrical double layer on the particle surface, which leads to a decrease of the total area that could be stabilized.

The uniformity of the particles formed via surfactant-free emulsion polymerization proves that once the nucleation took place, no secondary nucleation is possible and the main locus of
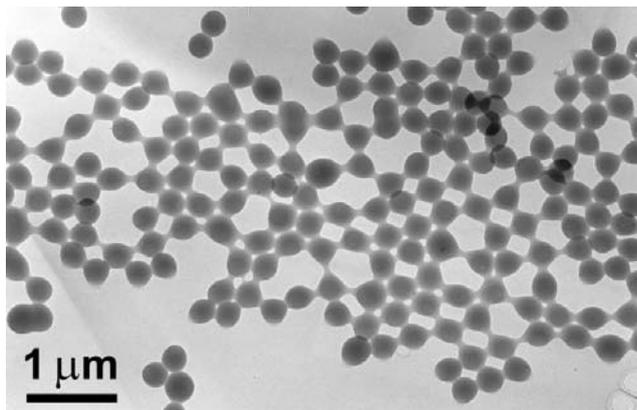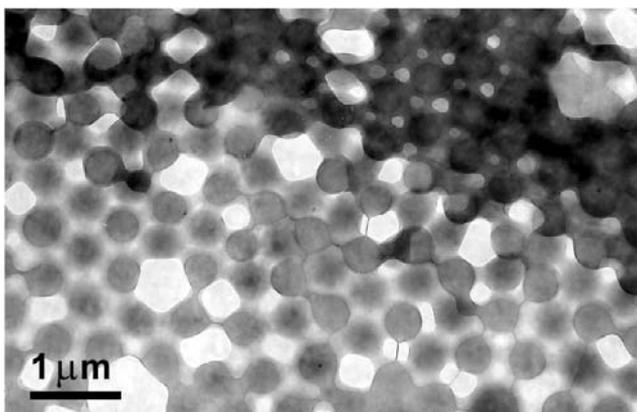
polymerization is represented by the particles swollen with monomer. Indeed, taking into account that the critical nucleation degree of polymerization[21] (j_{cr}) for PVAc oligomeric radicals is about 20, and the length at which macroradicals enter the particles[22] (z) is approximately 8, one can conclude that, the growing oligoradicals will enter the existing particles before they reach the length required to lose water solubility.

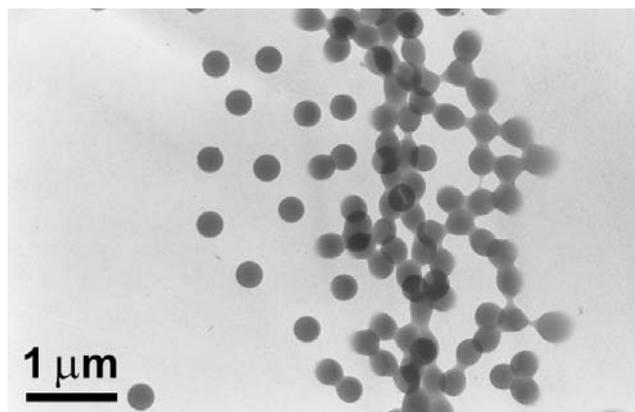Fig. 2 – TEM image for latex L1 prepared with 0.6 wt.% KPS.

Fig. 3 – TEM image for latex L1 prepared with 1.0 wt.% KPS.

Fig. 4 – TEM image for latex L1 prepared with 1.4 wt.% KPS.

Adsorption of surfactants onto PVAc particles

The Py fluorescence was used to detect changes in micropolarity of the probe's immediate environment.[23-25] Thus, the changes in the ratio of the intensities of the first and the third vibronic

bands, I_1/I_3, located near 373 and 384 nm, respectively, offer information about the modifications in the micropolarity of the Py environment: a high micropolarity sensed by Py is associated with a high I_1/I_3 value, while an increased hydrophobicity of the microdomains in

the close vicinity of Py molecules results in a low value for I_1/I_3. Nevertheless, Py molecules, due to their hydrophobicity, will tend to occupy the hydrophobic microdomains resulted from the self-association process in surfactant systems.

The dependence of I_1/I_3 ratio on the concentration of SDS and Brij 56 (polyethoxylated alcohol with 10 ethoxy groups and 16 carbon atoms in the alkyl chain) at different temperatures is presented in Fig. 5. These etalon curves can be accurately fitted by a Boltzmann reverse sigmoid, from which the *cmc* of surfactant is considered as the inflection point as follows:

$$\frac{I_1}{I_3} = (I_1/I_3)_{\min} + \frac{(I_1/I_3)_{\max} - (I_1/I_3)_{\min}}{1 + \exp\left(\dfrac{\log[surf] - \log cmc}{b_{surf}}\right)} \tag{2}$$

where $(I_1/I_3)_{\min}$ and $(I_1/I_3)_{\max}$ are the upper and the bottom limits of the sigmoid, [surf] is the concentration of surfactant, and b_{surf} is a parameter which describes the steepness of the curve (its high value denotes a shallow curve).

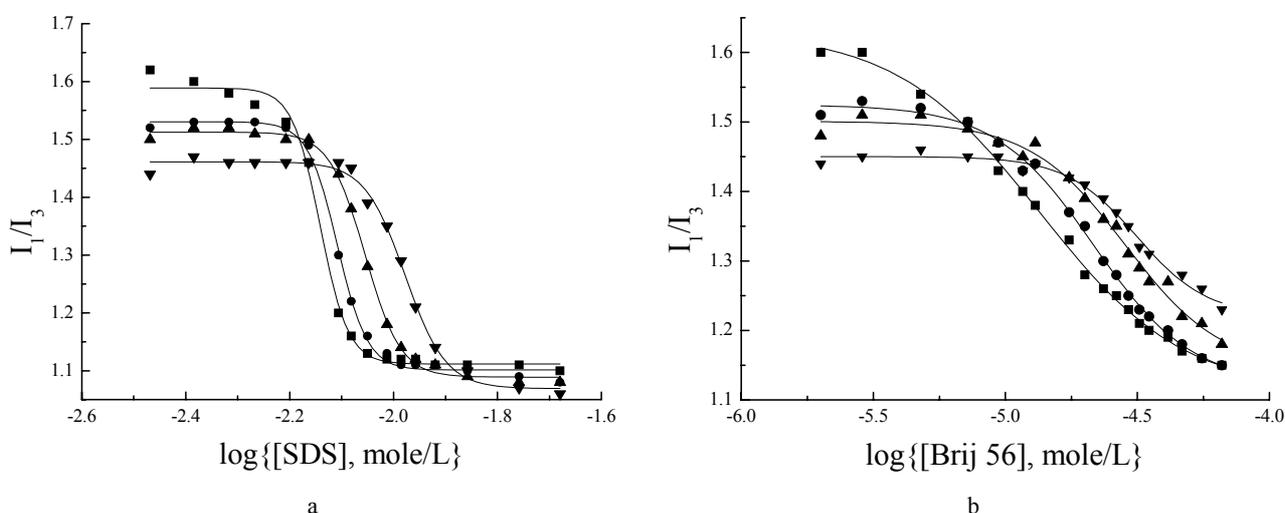Fig. 5 – Ratio I_1/I_3 for SDS (a) and Brij 56 (b) at different temperatures: 23 (■); 40 (●); 55 (▲) and 70^0C (▼).

As the temperature increases, the shape of sigmoids remains almost unchanged for SDS, although a decrease of the height of the sigmoid can be observed for both SDS and Brij 56. For the two surfactants, *cmc* values increase as the temperature rises, as can be seen in Table 2. For SDS the increase of *cmc* is not very significant at low temperatures, but at the highest temperature it reached 46% with respect to the lowest *cmc* value, which cannot be negligible. On the contrary, the temperature effect on *cmc* in the case of the nonionic surfactant is considerably higher at lower temperatures. For example, rising the temperature from 23 to 40^0C induces an increase of *cmc* of about 60%, whereas a further increase in temperature leads to a less pronounced influence.

Table 2

The *cmc* values and area of adsorbed molecule of surfactant for SDS and Brij 56 at different temperatures

Temperature (^{0}C)	SDS		Brij 56	
	cmc (mM)	a_s, (nm^2)	*cmc* (μM)	a_s, (nm^2)
23	7.22	1.03	13.47	25.04
40	7.80	1.32	21.55	22.75
55	8.81	1.86	28.53	20.12
70	10.52	-	31.43	30.53

The effect of temperature on the self-assembly of surfactants in aqueous medium is complex due to the opposite phenomena that take place as the temperature increases. On the one hand, there is a

decrease of the hydration of the hydrophilic groups, which favors micellization. On the other hand, the arrangement of water around the hydrophobic tails is deeply destroyed, an effect that has an unfavorable influence on micelle formation. The findings arisen from the studied systems (Table 2) show that the temperature effect is much more pronounced in the case of non-ionic surfactant and in spite of the general rule that their *cmc* has a monotonic decrease with increase of temperature,[3] the *cmc* of Brij 56 shows an opposite effect.

The adsorption studies were realized on latex L2 having an average particle diameter of 300 nm. Assessment of the adsorption of surfactants onto PVAc particles at different temperatures leads to a_s values by use of eq. 1. Since the amount of SDS adsorbed at 70^0C could not be determined with satisfactory accuracy, a_s value could not be calculated.

Although *cmc* increases with temperature for both surfactants, the area occupied by adsorbed surfactant molecules on PVAc particles exhibits different tendencies: there is an expected increase of a_s with temperature for SDS, showing that the polymer particles adsorb less surfactant at higher temperatures, while, for Brij 56, there is a decrease of a_s for temperatures below 55^0C, followed by an unexpected increase at 70^0C. The amphipathic character of non-ionic surfactant at molecular level, consisting of both hydrophilic and hydrophobic portions, behave differently as the temperature increases: the polyoxyethylene chain progressively loses its hydration water, decreasing in its overall size, which favors the closer packing in the adsorbed layer, while the hydrocarbon chain becomes less compact, occupying a larger surface onto particles. The relative magnitude of these two opposite effects determines the variation of a_s values over a studied temperature range.

CONCLUSIONS

Stable latices of PVAc with a narrow particle size distribution were prepared via batch surfactant-free emulsion polymerization using different concentrations of KPS as initiator. As the concentration of initiator increases, the maximum conversion and rate of polymerization increase. At the same time, the higher KPS concentrations, the larger particles are obtained. This is in accordance with a lower overall particle surface to be

electrostatically stabilized under the increasing of the ionic strength of the systems.

The uniform particles were used as a model surface for studying surfactant adsorption. The use of pyrene as a hydrophobic fluorescent probe is a suitable spectroscopic tool for investigation of self-assembly process of various types of surfactants during their micellization or adsorption onto polymer surfaces.

The temperature influence on both micelle formation and adsorption of SDS onto PVAc particles shows that the rise of temperature in the range of $23\text{-}70^0C$ causes the increase of *cmc* in solution, simultaneously with a_s values.

Thermal behavior in the case of Brij 56 reveals some interesting aspects. As the temperature rises, *cmc* increases with a rate which progressively diminishes, whereas a_s has a decreasing tendency. These are due to the complex influence of water-surfactant interaction (dehydration of polar groups, randomization of water molecules arrangement around the hydrophobic tails) on micelle formation and adsorption phenomena.

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