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Influence of interfacial properties of styrene/butadiene latex on the interaction with poly(vinyl alcohol) in aqueous media

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Abstract The interfacial properties of styrene/butadiene latex were found to play a substantial role in its interaction with partially hydrolysed polyvinyl acetate (PVOH/Ac) in aqueous solutions. In particular, the level of carboxylation of the latex particles governs the adsorption process. A slightly hydrophobic PVOH/Ac is weakly adsorbed onto medium carboxylated latex at low equilibrium concentrations, whereas a multilayer adsorption occurs at high polymer concentrations, closely resembling the incipient phase separation already observed in the case of PVOH/Ac–polystyrene latex systems. The adsorption mechanism for the monolayer formation is suggested to be of entropic origin, driven by the hydrophobic interactions between the latex surface and especially the acetate groups of the PVOH/Ac chain. Increasing the hydrophilic character of the latex surface through pre-adsorbed sodium dodecylbenzene sulphonate or non-ionic fatty alcohol ethoxylate surfactants did not significantly affect the association behavior between PVOH/Ac and the latex surface. In addition to the importance of the interfacial properties of the latex particles, it has been shown that an increased degree of hydrolysis of the PVOH/Ac macromolecule also leads to an appreciable reduction in its affinity for the styrene/butadiene latex interface.

Keywords Latex · Calorimetry · Enthalpy · Poly(vinyl alcohol) · PVOH · PVOH/Ac · Carboxylation · Zeta potential · Styrene/butadiene · Glass transition temperature

Introduction

Various types of latices are used in pigment coating dispersions such as paints and paper coating dispersions in order, after drying, to provide surface strength through particle–particle and particle–substrate interactions. The industrial latex emulsions used for paper applications are manufactured from vinylic monomers such as styrene, butadiene, acrylics, and acetates [1]. The latex particles are usually tailored to possess a certain final quality while maintaining colloidal stability during the application. The latter is especially important for high-solids coating dispersions, where stability against flocculation under high shear rates and at high electrolyte concentrations must be considered. The stability of latex particles in such multi-component complex suspensions is usually enhanced through surface modification by increasing the number of charged groups and/or by the addition of stabilizing agents. Charged groups, which give the electrostatic stability, are usually achieved either by incorporating ionic emulsifiers or by using an ionogenic co-monomer during the latex synthesis [1]. Steric stability is obtained with an adsorbed layer of non-ionic surfactants or macromolecules, which prevent flocculation because of steric hindrance [2]. The mechanism for stabilization of the latex particles should be carefully selected, since it may affect not only the colloidal stability of the suspensions but also the application process and the properties of the final coated layer.

Water-soluble polymers are frequently used to stabilize colloidal latex particles against flocculation in aqueous media. The fully hydrolysed polyvinyl acetate, i.e. poly(vinyl alcohol) (PVOH), and a partly hydrolysed polyvinyl acetate (PVOH/Ac) have been used quite extensively and they fulfil an important function in technical dispersions. For instance, PVOH/Ac has been used in the emulsification of styrene [3, 4]. For this reason, fundamental studies have been carried out concerning the mechanisms of interaction between polystyrene latex and PVOH/Ac. The temperature dependence [5], the influence of solvency [6], and the effect of the degree of hydrolysis (vinyl alcohol/vinyl acetate ratio) [7, 8] on the adsorption mechanism have been given special attention. Van den Boomgard et al. [5] found no significant changes in the amount adsorbed with increasing temperature and that the adsorption isotherm of PVOH/Ac on polystyrene revealed a multilayer adsorption. They suggested that the first adsorbed layer was related to the hydrophobic nature of the polystyrene and that the subsequent development of a multilayer was the result of an incipient phase separation of the PVOH/Ac at the latex–solution interface [5]. They also observed a decreasing solubility of the PVOH/Ac with increasing temperature [5], which can be explained as being due to a phase separation process because of the presence of fractions with high acetyl contents [4, 5]. Barker and Garvey [6] used an extra salt (sodium sulphate anion) to study the solvency influence through a salting-out effect instead of the temperature dependence. They found that the hydrophobic acetate groups are the adsorbing segments of the polymer, which is consistent with the other results [4, 5, 7]. In addition, Croot et al. [7] concluded that the polydispersity, the molecular mass, and the distribution of acetyl groups on the polymer chain play a substantial role in the affinity of the PVOH/Ac for the latex surface. Although it has been shown that the molecular mass did not significantly affect the amount adsorbed [5], van den Ven [9] stressed that, in practical cases, the adsorption onto surfaces might be kinetically (diffusion) rather than thermodynamically controlled. He demonstrated the importance of kinetics for the adsorption of a high molecular mass PVOH/Ac ($M=1.25\times10^5$) onto polystyrene latex. The rate of adsorption increases with increasing polymer concentration. As a consequence, the adsorbed macromolecules have more time to rearrange before new adsorbing species arrive when the polymer concentration is low. In the high concentration range, the adsorbed macromolecules retain a more coiled interfacial configuration [9, 10]. This observation is especially interesting, because it has also been stated [11] that the polymer does not exist in random coils in aqueous solution but as large polymer assemblies. Finally, it is important to be aware of the fact that the solubility of PVOH is dependent, for example, on the concentration and on the acetate content.

While the adsorption of PVOH and PVOH/Ac onto polystyrene has been widely studied, surprisingly few reports consider their adsorption onto copolymer latices such as styrene/butadiene. Most of the investigations presented are devoted to the interactions occurring in high-solids pigment coatings that usually contain several components and thereby represent particularly complex systems. It is probable that impurities and competitive adsorption play a significant role in the observed interactions. For example, the influence of surfactants on the adsorption process is particularly important, since it is evident that these affect the stability of the suspensions to a great extent. It has been shown that anionic surfactants interact with the PVOH/Ac through associations between the hydrophobic acetate groups of the macromolecule and the alkyl chains of the surfactants [4, 12, 13, 14, 15, 16]. On the other hand, no or only very weak interactions were found to occur between the non-ionic surfactants and PVOH/Ac [14].

The object of the present work was to investigate the influence of the interfacial properties of styrene/butadiene latex particles in aqueous media on their interaction with PVOH/Ac. The latex–PVOH/Ac interactions were monitored by means of Zeta potential, isothermal titration calorimetry, capillary viscometry, and adsorption measurements. The surface chemical properties of the latices, especially the hydrophilic–hydrophobic character of the surface, were modified through changes in the styrene/butadiene ratio and in the level of carboxylation. In addition, the influence of physically pre-adsorbed surfactants on the latex–PVOH/Ac interactions was also studied. Finally, the effect of fully and partly hydrolysed polyvinyl acetate on the interactions with the latex surfaces were compared.

Experimental

Materials

Five different styrene/butadiene latex samples were supplied by Dow Chemicals Inc. (Horgen, Switzerland). Two of these were latices with a low degree of carboxylation (SB01 and SB03) and two with a high degree of carboxylation (SB02 and SB04). The level of carboxylation of the latex particles (SB01-SB04) was adjusted by using different amounts and types of vinylic acids. Different surfactants were used to stabilize the latex particles. For example, the very low carboxylated SB01 grade contained high levels of an anionic sodium dodecyl sulphonate (SDS) surfactant.

Since the latex emulsions contained quantities of surfactant molecules, a medium carboxylated latex, substantially free of surfactants (SB05), was used as a reference. An anionic surfactant, a non-ionic surfactant, and a mixture of both these surfactants were added to the SB05 latex emulsion to give the samples SB06, SB07, and SB08, respectively. The surfactants used were an anionic linear dodecyl benzene sulphonate sodium salt (SDBS) (MARANIL A 25, Henkel GmbH, Germany) and a non-ionic fatty alcohol ethoxylate surfactant (AE) (Lutensol TO89, BASF, Germany), with the general formula $RO(CH_2CHO)_8H$ where R denotes $i\text{-}C_{13}H_{27}$. The amount of surfactant added to the latex emulsions was 1 wt% calculated on the weight of latex particles. Since it is known that the adsorbed amount of surfactant is greatly affected by the hydrophobic properties of the latex, it is reasonable to expect that the pre-adsorption of a surfactant on the latex surface increases the hydrophilic character of the latex particles [12, 17, 18, 19]. The particle size was found to be close to 0.14 μm for all the investigated latex particles (when determined with a light scattering technique). Abbreviations used for the latices and the related information are summarized in Table 1. All chemicals were used without further purification.

Two different grades of poly(vinyl alcohol)s supplied by Clariant GmbH (Germany) were used. The polymer with a low degree of hydrolysis (saponification) was an 87.7 ± 1.0 mol% hydrolysed polyvinyl acetate, PVOH/Ac, (Mowiol 4–88) with a residual acetyl content of 10.8 ± 0.8 wt% and an average molar mass of 31,000 g/mol. The poly(vinyl alcohol) was a 98.4 ± 0.4 mol% hydrolysed polyvinyl acetate (Mowiol 4–98) with a residual acetyl content of 1.5 ± 0.4 wt% and an average molar mass of approximately 27,000 g/mol. The technical data for the PVOH and PVOH/Ac are based on information provided by the supplier. In order to ensure complete dissolution of the polymer, the dry polymer granules were dissolved in an aqueous 0.01 M NaCl solution to a final concentration of 10 wt% (unless otherwise stated) and then heated to 365 K for approximately 50 min under continuous stirring. The measurements were obtained using relatively fresh polymer solutions (1–3 days) in order to avoid changes in conformation and solubility due to ageing [20].

Zeta potential measurements

The electrophoretic mobility of the latex suspensions was determined as a function of added PVOH or PVOH/Ac. From the 1 wt% latex suspensions, a small amount of the suspension was taken and diluted in a 0.01 M NaCl solution prepared from distilled Millipore water. After reaching a stable pH value of 8.5, the electrophoretic mobility of the dilute latex suspension (approximately 0.01 wt%) was determined using a Malvern Zetasizer3000 (Malvern Instruments Inc.). The Helmholtz–Smoluchowski equation was then used to calculate the Zeta potential from the electrophoretic mobility data.

Isothermal titration calorimetry measurements

The enthalpy changes accompanying the adsorption of polymer onto latex particles were measured using an isothermal titration calorimeter (TAM 2277, Thermometric AB, Sweden). Small amounts of a 1 wt% polymer (PVOH, PVOH/Ac) stock solution were injected stepwise into the reaction vessel containing the 1 wt% latex suspensions prepared as described above. A portion of the homogeneous latex suspension (3 g) was introduced into the calorimetric vessel (volume = 4 cm^3) and stirred at 120 rpm. The amplifier range was 100 μW and 30 injections were performed during the experiments. The enthalpies of interaction, ΔH_r, associated with the subsequent adsorption steps, and thereby corresponding to a change in the adsorbed phase during its formation, were calculated from the experimentally measured enthalpy changes according to:

$$\Delta H_r = \Delta H_{obs} - \Delta H_{dil(l)} \tag{1}$$

where ΔH_{obs} denotes the observed (experimental) enthalpy and $\Delta H_{dil(l)}$ is the enthalpy of dilution. Dilution experiments were performed by injecting small amounts of the stock solution into a 0.01 M NaCl aqueous solution in order to obtain a value for the enthalpy of dilution, $\Delta H_{dil(l)}$. (Low enthalpic effects were obtained when the polymer was diluted.)

Adsorption measurements

Adsorption isotherms were determined for the PVOH/Ac on the medium carboxylated latex substantially free of surfactant (SB05). The initial concentrated suspension of latex particles was diluted to 1 wt% in an aqueous 0.01 M NaCl solution. The pH value was adjusted to 8.5 by the addition of small amounts of sodium hydroxide (Aldrich) and the temperature was maintained at 298 ± 2 K. After addition of PVOH/Ac (a given volume of the 10 wt% solution), the suspension was gently stirred for 20 h until equilibrium adsorption was attained. The liquid phase was then removed by a suspension method (or by serum exchange), i.e. filtering through a 0.1 μm membrane under stirring (NC 10, Schleicher & Schuell, Germany) and the clear equilibrated supernatant phase was analysed by UV–Vis spectroscopy (λ = 670 nm), according to the method of Zwick [20], to determine the non-adsorbed polymer content.

Kinematic viscosity measurements

The kinematic viscosity, ν_{kin}, was measured using an Ubbelohde capillary viscometer (Nr. 501 01/0a, Schott Geräte GmbH, Germany), on the latex suspensions with and without the added macromolecule. The suspensions were prepared in the manner

Table 1. Latices used in this study

Latex	T_g (°C)	Carboxylation	Surfactant	Charge[a]
Styrene/butadiene, (SB01)	–17	Very low	[b]	0.15
Styrene/butadiene, (SB02)	–7	High	[b]	0.73
Styrene/butadiene, (SB03)	23	Low	[b]	0.42
Styrene/butadiene, (SB04)	25	High	[b]	0.63
Styrene/butadiene, (SB05)	7	Medium	No	0.55
Styrene/butadiene, (SB06)	7	Medium	SDBS	0.55
Styrene/butadiene, (SB07)	7	Medium	AE	0.55
Styrene/butadiene, (SB08)	7	Medium	SDBS + AE	0.55

[a] Estimated level of carboxylation in meq/g based on the amount of added acid (0.4 is usually considered to be a low and 0.8 a high degree of carboxylation)

[b] Commercial grades of latex emulsions that contain emulsifying agents and post-added surfactants originating from the manufacturing process

described above and the kinematic viscosity was then determined at 298 K. The value obtained was then used to calculate the reduced viscosity of the suspension in order to show the influence of the added polymer.

Results

Electrophoretic mobility and adsorption isotherms

Figure 1 shows the Zeta potential of styrene/butadiene latices SB01–SB04 at different concentrations of the partly hydrolysed polyvinyl acetate (PVOH/Ac). It can be seen that the Zeta potential is less affected by the addition of PVOH/Ac in the case of the highly carboxylated lattices, SB02 and SB04, than in the case of the low carboxylated lattices, SB01 and SB03. In the latter case, the effect on the Zeta potential is very slight at low PVOH/Ac concentrations (0.01–0.02 g/g_{latex}). At higher concentrations, the Zeta potential levels out to a value of approximately –20 mV.

The results presented in Fig. 2 show both the adsorption isotherm of partly hydrolysed PVOH/Ac on a medium carboxylated latex substantially free from surfactants (SB05) and the Zeta potential values of the latex particles following the adsorption. This was done in order to evidence the relationship between adsorption capacity and Zeta potential. The adsorption isotherm shows a weak initial adsorption typically ascribed to a weak affinity of PVOH/Ac for the latex surface. At higher equilibrium concentrations (> 2.5 mg/ml), the adsorption increases steeply without reaching of any saturation plateau.

The Zeta potential values show a linear increase in the initial region up to approximately 1.8 mg/ml. The change in Zeta potential is less pronounced with a further increase in the PVOH/Ac concentration and levels out to approximately –7 mV.

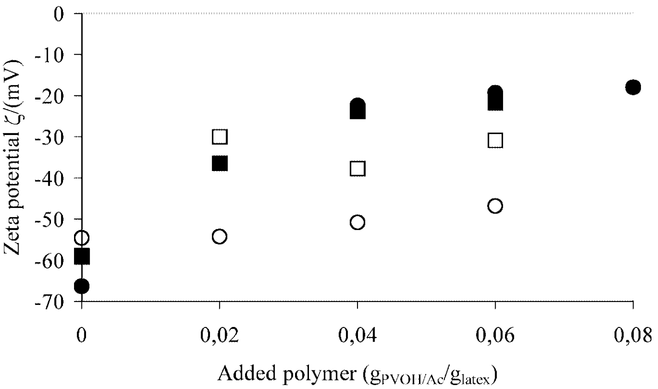

Fig. 1. Zeta potential determined for styrene/butadiene lattices at different concentrations of the PVOH/Ac: (filled circle) SB01, (open circle) SB02, (filled square) SB03, and (open square) SB04

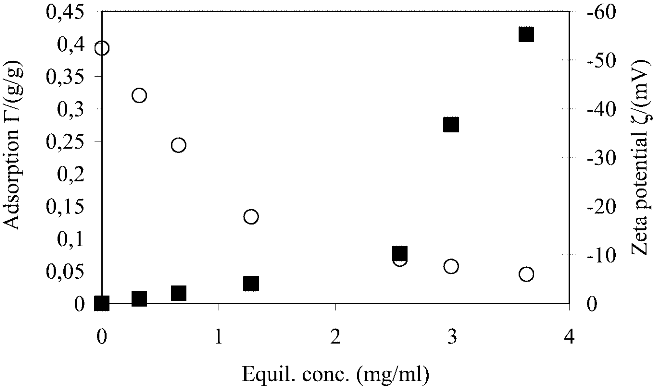

Fig. 2. Adsorbed amount (filled square) and Zeta potential (open circle) plotted versus equilibrium concentration demonstrating the interaction between the medium carboxylated latex (SB05) and the PVOH/Ac

Enthalpy of interaction

The calorimetric curves presented in Fig. 3 show the enthalpy of interaction, ΔH_r, for PVOH/Ac and latex samples (SB01–SB04). The calorimetric results were obtained by injecting a 1 wt% stock solution of PVOH/Ac into a 1 wt% latex emulsion. The observed enthalpy change was corrected for the enthalpy of dilution in order to give the net enthalpy change reflecting the interaction between the latex emulsion and PVOH/Ac. The curves in Fig. 3 show that injection of PVOH/Ac solution into the latex emulsions yields an exothermic effect. A substantially higher (in absolute terms) enthalpy change is obtained with the very low carboxylated latex (SB01) than with samples SB02, SB03, and SB04. The exothermic effect is initially very high and ends when approximately 0.08 g/g_{latex} PVOH/Ac has been added. In the case of latices SB02–SB04, the difference is

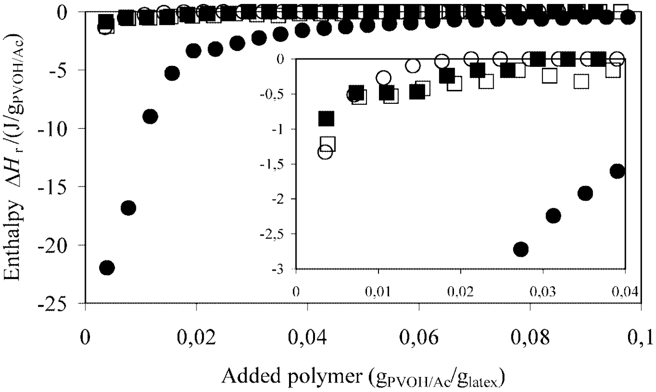

Fig. 3. Enthalpy of adsorption observed when adding PVOH/Ac to styrene/butadiene latices: (filled circle) SB01, (open circle) SB02, (filled square) SB03, and (open square) SB04

less significant and the exothermic effect levels out at approximately 0.02–0.04 g/g_{latex} of added PVOH/Ac.

Figure 4 shows that exothermic enthalpy changes were also observed in the case of the latex substantially free from surfactants. This agrees well with the data presented in Fig. 3. Exothermic enthalpy changes were observed with the latex samples containing an anionic surfactant (SB06), a non-ionic surfactant (SB07), or both anionic and non-ionic surfactants (SB08). However, these thermal effects are rather small and exhibit a fairly high scatter. The curves also indicate that the enthalpy changes are slightly declining.

Reduced viscosity in relation to Zeta potential measurements

Figure 5 shows the reduced viscosity plotted versus the Zeta potential for the medium carboxylated latex emulsion with different concentrations of PVOH/Ac. The data are reported for latex samples without (SB05) and with surfactants (SB06–SB08) in order further to analyse the calorimetric results presented in Fig. 4. The results show that an increase in polymer concentration from approximately 0.22 mg/ml to approximately 2.26 mg/ml is associated with a reduction in Zeta potential to –35 mV. The lowest concentration of the PVOH/Ac is thus reflected by the lowest Zeta potential values (approximately –63 mV), while the highest level of addition corresponds to the highest Zeta potential values (approximately –35 mV). This total change in Zeta potential is thus the same in all cases. However, obvious differences are observed in the reduced viscosity, particularly at low polymer concentrations, i.e. the first three points of the respective curves. The latex suspension without surfactant shows an overall increase in reduced viscosity, whereas the latex emulsions with anionic or non-ionic surfactant show a decrease in reduced viscosity at low polymer concentrations, which levels out to a constant value at higher polymer concentrations. The latex emulsions with both anionic and non-ionic surfactants show high values of the reduced viscosity at both low and high polymer concentrations.

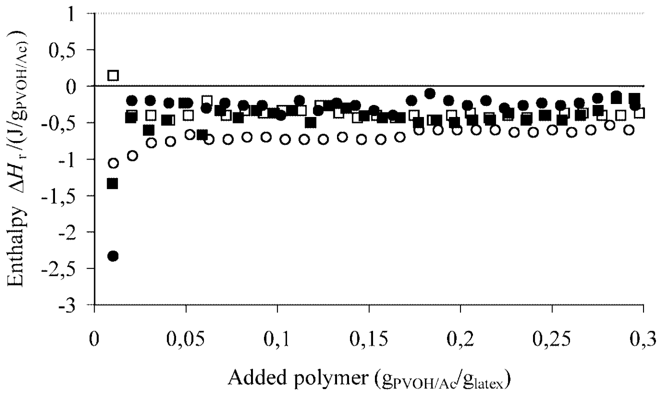

Fig. 4. Enthalpy changes showing the interaction between the PVOH/Ac and the medium carboxylated latex pre-treated with different surfactants: (filled square) SB05, (filled circle) SB06, (open circle) SB07, and (open square) SB08

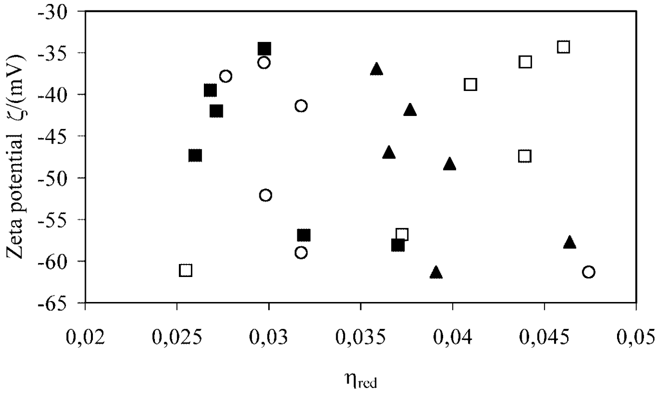

Fig. 5. Zeta potential plotted versus reduced viscosity, η_{red}, for latex suspensions with different amounts of the partly hydrolysed polyvinyl acetate, demonstrating the influence of surfactants: (open square) SB05, (filled square) SB06, (open circle) SB07, and (filled triangle) SB08

Finally, Fig. 6 demonstrates the difference between a fully hydrolysed polyvinyl acetate (PVOH) and a partly hydrolysed polyvinyl acetate (PVOH/Ac) in association with the medium carboxylated latex (SB05). It is evident from the graph that the fully hydrolysed polymer does not change the Zeta potential of the latex particles, whereas its hydrophobic analogue show an increases in the Zeta potential when the polymer concentration is increased. Thus, in the non-associating case, a linear decrease in the reduced viscosity of the suspensions is observed with increasing concentration of PVOH,

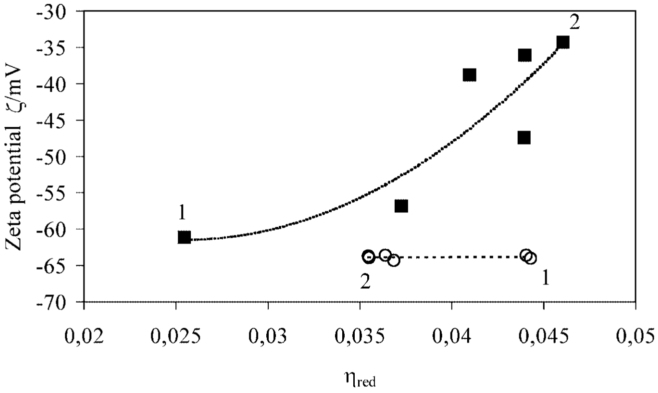

Fig. 6. Zeta potential plotted versus reduced viscosity for emulsions of the medium carboxylated styrene/butadiene latex (SB05) at different concentrations of (filled square) PVOH/Ac and (open circle) PVOH. The numeral (1) represents low polymer concentrations (0.22 mg/ml), while the numeral (2) represents high polymer concentrations (2.26 mg/ml)

whereas the opposite trend is evident with the more hydrophobic PVOH/Ac polymer.

Discussion

Mechanism of adsorption of PVOH/Ac

The adsorption of the PVOH/Ac on the medium carboxylated latex shows an interesting feature. The adsorption isotherm in Fig. 2 exhibits first a saturation plateau at a low concentration indicating a very weak affinity between the surface of styrene/butadiene latex particles and PVOH/Ac, with adsorbed amounts in the same range as those observed on polystyrene [5]. The subsequent adsorption layer, on the other hand, resembles the incipient phase separation suggested by Van den Boomgaard et al. [5]. The SB05 latex, substantially free of surfactants, can be considered to be a relatively hydrophobic surface containing a few hydrophilic sites in the form of carboxylic acid groups. The results and shapes of the curves are thus in agreement with results presented for PVOH/Ac–polystyrene systems [5]. It can, therefore, be assumed that the formation of the monolayer at low equilibrium concentrations is governed by the dispersive (hydrophobic) interactions between the hydrophobic acetate groups of the macromolecular chain and the hydrophobic fraction of the latex surface. It is probable that this mechanism of adsorption is associated with an exothermic enthalpy change as indicated by the calorimetric data (Figs. 4 and 5). Indeed, it is reasonable to assume that the observed exothermic effect arises from a dehydration of both the hydrophobic acetate groups of the macromolecule and the hydrophobic sites on the latex surface.

The fairly weak amount adsorbed at very low concentrations indicates that the adsorption is partly hindered. This is probably due to the presence of some charged and hydrophilic carboxylate groups on the SB05 latex surface. This is in agreement with the theories proposed by Kronberg and Stenius [17], which state that an increase in the surface polarity of the latex particles leads to a decrease in the adsorption of hydrophobic molecules. The subsequently adsorbed layer may be explained by the statements of Van den Boomgard et al. [5] who suggested a strong adsorption of the first layer followed by a phase separation of the PVOH/Ac. A similar situation involving a phase separation at the interface in the present system seems reasonable. On the other hand, we cannot neglect the indications that the initial polymer concentrations affect the amount adsorbed and that the polymers are probably adsorbed as large aggregates [9, 10, 21].

Figure 2 also shows that the relationship between the Zeta potential and the adsorbed amount is different at low and high polymer concentrations. At low polymer concentrations (<2 mg/ml), a fairly linear dependence is observed between the amount adsorbed and the Zeta potential (effective surface charge). The breakpoint at approximately -10 mV is fairly distinct and clearly demonstrates that the shear plane is not significantly changed even when the amount of polymer adsorbed is more than four times as large. It can, however, be assumed that there is a significant change in polymer conformation, because a further addition of PVOH/Ac does not significantly change the Zeta potential.

It is interesting to notice that, at high levels of addition of PVOH/Ac, the concentration corresponds to 0.35–0.85 wt% calculated per mass of solution assuming that there is no adsorption. Since the PVOH/Ac was prepared as a highly concentrated initial solution (15 wt%), it is probable that large polymer aggregates are present in the solution and that these might adsorb onto the latex surface. This may explain the relationship between the amount adsorbed and the Zeta potential, i.e. the subsequent layer is predominantly an adsorption of large assemblies, which do not spread out over the surface. This makes the transition from dilute to semidilute polymer concentrations interesting, since the critical concentration regime (c^*) might be responsible for the occurrence of a threshold value for the multilayer adsorption. However, the solubility properties of PVOH/Ac and PVOH in aqueous media should also be considered, particularly with regard to the concentration and the vinyl acetate content (degree of hydrolysis). Finally, as discussed by Fleer et al. [22], the adsorption of uncharged polymers onto charged surfaces is affected by the counter ions. These ions will compete with the polymer segments and may act as a displacer if the Stern potential is sufficiently high [23]. The effect of the counter ions is not revealed in this work, but it can be assumed that sodium and chloride ions in the double layer will play a minor role for the adsorption process compared to the hydrophilic character of the surface, at least at low electrolyte concentrations [24, 25].

Influence of the degree of carboxylation of latex on the interaction with PVOH/Ac

It has been reported in several papers that the hydrophilic–hydrophobic character of the latex surface has a remarkable influence on the amount of hydrophobic molecules adsorbed [5, 7, 12, 13, 14, 15, 16, 17, 18]. The relevance of this statement related to PVOH/Ac–latex systems can be concluded from the Zeta potential and calorimetric results presented in Fig. 1 and Fig. 3, respectively. This suggests, according to the calorimetric results, that the affinity of the PVOH/Ac for the very low carboxylated latex SB01 is much higher than that for, for example, the high carboxylated latices SB02 and

SB04, at least at low polymer concentrations. Similar conclusions may be drawn from the Zeta potential measurements, which suggest a much higher affinity between the low carboxylated latices (SB01 and SB03) and PVOH/Ac. When the two low carboxylated latices are compared, a significant difference in enthalpy is seen in the case of SB01, whereas the SB03 does not show similar magnitudes in exothermic effects, even though the Zeta potential values for both latices approach the same end value at high polymer concentrations. It must, however, be stressed that interaction may occur, for instance, in the bulk solution between PVOH/Ac and surfactants, and this may yield significant thermal effects as was earlier reported for PVOH/Ac and SDS [4]. However, although surfactant–PVOH/Ac association may occur in the bulk solution and/or surfactant molecules may be displaced from the latex surface, these data reveal that there is a relationship between the degree of carboxylation of the latex particles and their interaction with the slightly hydrophobic PVOH/Ac.

The role of latex chemistry in the association with PVOH/Ac

To our knowledge, no study has been presented concerning the influence of the level of co-monomers in co-polymers such as styrene/butadiene latices on the interaction with PVOH/Ac. In the present study, the co-monomer composition, i.e. styrene/butadiene ratio, was also investigated. A high butadiene content is known to give a soft latex particle, i.e. a low glass transition temperature, whereas styrene itself is known for the opposite effect [1]. Thus, the mixture of the above-mentioned monomers will give latex particles (or latex films) with certain desired physical properties when dried. In aqueous media, however, it is generally accepted that the styrene to butadiene ratio does not affect the interfacial properties to an appreciable extent. From these results it is rather difficult to find any direct correlation between the monomer composition of the latex and the observed interactions. Since both the styrene and butadiene are themselves fairly hydrophobic, no significant differences in the interaction behaviour are to be expected. However, the high enthalpy change observed for SB01 compared with the SB03 latex indicates that the increase in butadiene content favours the interaction with the PVOH/Ac. The SB01 sample is much less carboxylated than SB03, and this explains the much larger observed enthalpy changes. Moreover, it appears from the change in Zeta potential values that there is no substantial difference between the low carboxylated latices (at high concentrations of PVOH/Ac) in terms of adsorbed polymer and its effect on the Zeta potential. The opposite is indicated for the latex samples with a high level of carboxylation, i.e. a stronger interaction with the SB04 than with the SB02. It is assumed that the latex composition (styrene to butadiene ratio) has a less marked influence on the interaction properties in aqueous media. The interfacial properties of the exposed latex surface, i.e. latex–water interface, will consequently play the most significant role in the latex–polymer interaction behaviour.

The role of surfactants on the adsorption and association in bulk solution

The role of surfactants, physically pre-adsorbed on the latex particle and/or in the bulk solutions, in the latex–PVOH/Ac association was also clarified. The latex surface (SB05) was modified by a pre-adsorbed surfactant in order to investigate the influence of the hydrophobic–hydrophilic character of the surface on the interaction behaviour with PVOH/Ac as previously described. Anionic sodium dodecylbenzene sulphonate sodium salt (SDBS) and/or a non-ionic fatty alcohol ethoxylate were pre-adsorbed onto the medium carboxylated latex prior to the addition of the PVOH/Ac in suspension. A separate work, using calorimetry and adsorption measurements, demonstrated that the surfactants were adsorbed onto the latex surface.

The calorimetric, Zeta potential, and viscometric data, presented in Figs. 4 and 5, strongly suggest that the pre-adsorbed surfactants do not significantly affect the adsorption of PVOH/Ac. This is deduced from the reduction in the Zeta potential observed for SB05–SB08 at high polymer concentrations, where, in all cases, the decrease in the Zeta potential is of similar magnitude. Thus, adsorption occurs on the latex particles although surfactants are pre-adsorbed, which can be taken as an indication of preferential adsorption of PVOH/Ac chains and probably a displacement of surfactant molecules. It can further be assumed that the surface interaction is more favoured with PVOH/Ac than with SDBS because of the absence in this case of electrostatic repulsion.

These findings are interesting, since the opposite has been documented for the adsorption of hydroxyethylcellulose on polystyrene. In that case, pre-adsorbed anionic SDS [26] or non-ionic (Trition X-405) [27] surfactants decreased the adsorption of hydroxyethylcellulose. The high concentration of surfactants (8.33 wt%) used in these studies might, however, explain the lower affinity observed. It is probable that all hydrophobic moieties on the macromolecule were occupied by the surfactants whilst in the bulk phase and thus not accessible for the adsorption. In the present work, much smaller quantities of surfactants were used (1 wt%), and this leaves more sites on the macromolecule available for adsorption on the hydrophobic fraction of the latex surface. Moreover, it can be assumed that the partly hydrolysed polyvinyl acetate is more hydrophobic than the cellulose derivative (hydroxyethylcellulose), and this explains the higher affinity for the latex.

As is evident in Fig. 3, thermal effects also occurred between the PVOH/Ac and the latex with pre-adsorbed surfactants. The enthalpy of dilution was measured in a 0.01 M NaCl solution and was found to be in the range of the background noise, i.e. $\Delta H_{\mathrm{dil(l)}} = 0$. This basically means that the enthalpy change, ΔH_{r}, corresponds to the total enthalpy change associated with all the adsorption and desorption processes on the latex surface as well as the interactions in the bulk solution between PVOH/Ac and surfactants. From the small differences obtained between the latex with and without surfactants it can be assumed that adsorption/association alone does not occur within the suspension. It has previously been suggested that weak or no interaction occurs between non-ionic surfactants and PVOH/Ac, and we can assume that the enthalpic effects obtained for PVOH/Ac and styrene/butadiene suspension containing non-ionic surfactant are due to adsorption of the macromolecule and displacement of the nonionic fatty alcohol ethoxylate surfactant. It can be assumed that the surfactants have no appreciable effect on the adsorption process on the latex surface, but their role in the bulk solution is more persistent and is predominantly related to a PVOH/Ac–surfactant association.

The data concerning the change in the reduced viscosity of the suspensions also indicate that an interaction probably occurs between surfactants and PVOH/Ac. The 1 wt% latex suspension free of surfactant (SB05) shows the lowest reduced viscosity at both low and high PVOH/Ac concentrations, whereas the latex suspension with the non-ionic surfactant, for example, shows the highest reduced viscosity value at low polymer concentrations (0.22 mg/ml). These differences can be ascribed to the surfactants and to the fact that polymer–surfactant association occurs in the bulk solution. In the case of the SDBS, it can be assumed that interactions occur similar to those suggested for sodium dodecylsulphate (SDS) and PVOH/Ac, i.e. mainly with the hydrophobic acetyl groups on the PVOH/Ac [13, 15]. It has also been concluded [4, 12, 13, 14, 15, 16] that PVOH/Ac forms complexes with SDS and that non-ionic surfactants exhibit a weak (or no) affinity with PVOH or PVOH/Ac.

These results are not sufficient to enable an adsorption mechanism for the latex surface treated with surfactants to be proposed, although it is probable that surfactants are displaced from the surface by PVOH/Ac. Since the Zeta potential of the suspension is not significantly changed by the pre-adsorption of surfactants, it is reasonable to attribute the difference in viscosity to the solvated properties of the particles [26] as well as to surfactant–PVOH/Ac interactions in the bulk solution.

The effect of degree of hydrolysis of the polyvinyl acetate

There is an interesting correlation between the degree of hydrolysis of the polyvinyl acetate and its interaction with the styrene/butadiene latex (SB05). The fully hydrolysed polyvinyl acetate, i.e. PVOH, does not change the Zeta potential, as would be expected in the absence of adsorption. According to Croot et al. [7], the hydrophobic acetyl groups are responsible for the adsorption process and PVOH shows no significant affinity for polystyrene latex. This is in agreement with the present results. It is possible that the stabilized polymer aggregates or molecules are strongly solvated, and that they are, therefore, less capable of participating in a hydrophobic interaction. The reduced viscosity data also reveal that the PVOH does not increase the viscosity of the latex suspension as much as was observed in the case of the PVOH/Ac (Fig. 6). The non-adsorbed PVOH can be regarded as a thickener between the particles in the bulk solution, which thereby increases the viscosity more or less linearly, whereas the PVOH/Ac predominantly affects the viscosity in terms of an increase in the hydrodynamic thickness of the particles (Stokes–Einstein). Note that at low polymer concentrations there is obviously a balance between screening of the surface charge, which decreases the solvated radius of the sphere, and the adsorbed polymer layers, which increase the hydrodynamic thickness.

Conclusions

It has been demonstrated that the interfacial properties of the latex particles play a key role in the interaction with PVOH/Ac in aqueous media. A weak initial adsorption was observed for the slightly hydrophobic PVOH/Ac macromolecules onto the styrene/butadiene latex, suggesting an adsorption mechanism mainly through hydrophobic (dispersive) interactions. A subsequent multilayer adsorption observed at high concentrations was ascribed not only to an incipient phase separation but also to the presence of large PVOH/Ac aggregates. It was also established that an increase in the hydrophilic character of the latex surface acts in two different ways. On the one hand, a higher concentration of surface carboxylic acid groups decreases the interaction with PVOH/Ac. On the other hand, increasing the hydrophilic character of the latex surface through the pre-adsorption of anionic or non-ionic surfactants did not significantly affect the adsorption capacity at the latex–water solution interface. This indicates that the adsorption of PVOH/Ac on latex is entropy-driven, and that pre-adsorbed surfactants are probably displaced. Although the interfacial properties of latex in aqueous media are highly important, these cannot be solely used to describe the adsorption process. Indeed it was also demonstrated that an increase in the degree of hydrolysis of the polyvinyl acetate decreases the amount of hydrophobic acetyl groups and thereby the extent of interaction with the hydrophobic part of the latex surface.

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