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ORIGINAL CONTRIBUTION

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Electrophoretic mobility evidence of surfactant partitioning in a waterborne latex

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Abstract In order to enhance substrate adhesion and pigment dispersion of fluorinated polymers, polyvinylidene fluoride (PVDF) type fluoropolymers are often used in combination with certain amounts of acrylics in paint formulations. We prepared an acrylic modified fluoropolymer (AMF) [1] latex by emulsion polymerization and monitored the effect of the addition of typical coalescents (TEX, DPM, DGB, and EGB) on the stability of an AMF latex. Both the effect on the bare latex and on surfactant post-added latex were investigated. No particular effect was noticed on the bare latex itself, but when surfactant is adsorbed initially to the particle surface, we observed surfactant partitioning between the polymer interface and the water phase, with different partitioning ratios depending on the coalescing solvent type. This leads to the presence of labile peaks in the electrophoretic mobility spectra and possible surfactant desorption from the AMF surface, with consequent latex destabilization.

Keywords Latex · Surfactant Electrophoretic mobility · Partitioning · Solvent-induced destabilization

Introduction

With the tightening of worldwide regulations on emissions of volatile organic compounds (VOC), latex-based products have found an increasing place in the paints and coatings market. Even though these formulations are mainly comprised of water, polymer, and pigments, many other components are added to the latex dispersion in order to target various end properties of the formulation itself (e.g., rheology, stability, wettability) and of the final film (e.g., coalescence, gloss, hiding, adhesion). Coalescence is one out of the many properties that are essential to film formation, but it is also a major limitation for air-dry latex paints. Coalescence only occurs if the film formation temperature is higher than the effective *Tg* of the polymer particles. However, the polymer film needs a high enough ultimate *Tg* to provide proper final properties (e.g., block resistance), so formulators use coalescing aids or coalescents to enhance particle coalescence during the drying process of latex paints. These coalescents soften the polymer particles, help them diffuse into one another when they come in contact, and then evaporate slowly out of the coating.

Understanding the effects of solvents on latex stability has been an active area of research in recent years. The swelling of latex particles by monomers and other solvents has been extensively studied, and the publications given as references are only a sampling of all that has been done [2, 3, 4, 5]. Vincent [6] also published in 1992 a review article detailing the coagulation kinetics of polystyrene latexes in n-alkanol/water mixtures. Most of these studies were done on model systems of polymer colloids, like polystyrene (PS) and its derivatives, and with common solvents like alcohols, chloroform, or toluene. In particular, Verdagan et al. [7] gave good insight on the hairy layer and co-ion enrichment models with their electrophoresis and

FTIR-ATR studies, and the articles from Galembeck et al. [8, 9, 10] show that there is a large increase in salt-induced coagulation which results from exposing the latex to solvent vapors, even though only small effects are observed on the particle's zeta potential. Furthermore, the Toronto Society for Coatings Technology (TOSCOT) investigated the impact on paint microflocculation of different variables, including coalescent type [11]. In fact, their results have shown that the use of a coalescent blend of hydrophobic/hydrophilic solvents rather than a strictly hydrophobic blend significantly reduced microflocculation or small size gels of high *Tg* styrenated acrylic emulsions.

Stability of a polystyrene latex as a function of 1-propanol concentration in the presence of electrolyte and surfactant was studied by Seebergh and Berg [12]. In all cases, zeta potential curves show a maximum as a function of the cosolvent, regardless of electrolyte or surfactant. Even though results seem correctly interpreted as a function of counterion displacement and change in medium dielectric constant, they lack time-dependant data.

However, to the best of our knowledge, no one has looked at the effect of various coalescents on the interactions between a surfactant and a polymer particle in a latex as a function of time. Since latex products used in the paint industry typically contain surfactants, the effect of the coalescing solvents on the surfactant–polymer interaction is of utmost importance when considering the shelf life of formulated paints.

Fluoropolymers are known to possess exceptional properties which can include UV stability, high durability and toughness, and non-stick surface properties. In order to improve the adhesion of fluoropolymers to their substrates, and to enhance pigment dispersion, a known amount of acrylic polymer is often included in the paint formulation [13]. For the present study, a PVDF-based latex was synthesized with a certain amount of acrylic to form an intimately mixed "acrylic modified fluoropolymer" or AMF latex [14]. Then, the electrophoretic behavior of the bare AMF latex particles, and of the particles with a post-added anionic surfactant, were monitored as a function of time after the addition of a solvent, using several types. We found that the electrophoretic properties of the bare latex are not significantly changed by the addition of solvent, but in the presence of surfactant, the spectra shift in a interesting manner which depends on the solvent type.

Experimental details

Latex

The AMF latex, with particles having a diameter of 96 nm, was extensively washed from residual additives and surfactants by ion-exchange and dialysis. Ion-exchange was done using a Bio-Rad AG 501-X8 mixed-bed resin. Dialysis was performed in SpectraPor 7, 50 000 MWCO cellulose membranes washed as described by the manufacturer. Dialysis was monitored by conductivity and stopped once the conductivity of the purified latex was stable for 2 consecutive days.

Chemicals

Ammonium lauryl sulfate (ALS), with a critical micellar concentration of 6.7×10^{-3} mol/L, served as surfactant during this whole study and was used as supplied by the manufacturer (Rohm and Haas). Coalescents were purchased from Eastman Chemicals and used as received: ethylene glycol butyl ether (EGB), diethylene glycol butyl ether (DGB), dipropylene glycol methyl ether (DPM) and 2,2,4-trimethyl-1,3-pentadiol mono(2-methylpropanoate) (TEX). Coalescents EGB and DGB are the most water-soluble, DPM has medium solubility and TEX is water-insoluble. At the concentrations studied, all but TEX are soluble in water

Electrophoretic light scattering

Electrophoretic mobilities were measured with the ZetaSizer 2000 unit from Malvern Instruments. All data was obtained in duplicate in a rectangular quartz cell. The samples were diluted to concentrations of 0.5% wt solids in water to obtain proper scattering intensities. Data was obtained at 25.0 ± 0.1 °C and at a pH of 8.5.

The measurement of coalescent effects on the electrophoretic mobilities was done as follows. To a 0.5% wt latex solution was added a constant amount of ALS. The amount of ALS was fixed at just over half the surface saturation concentration of the surfactant on the AMF, as determined by conductivity studies by the soap titration method [15, 16]: 1.96×10^{-5} mol of ALS/g of AMF compared to 3.68×10^{-5} mol/g for the saturation concentration [17]. Coalescents were then added individually to a known amount of [latex + surfactant] solution, at a level of 14–16% wt on the polymer, mixing manually to disperse the solvent. Finally, the electrophoretic variations of the ternary systems were monitored as a function of time and compared to the behavior of the bare latex in presence of the same amount of ALS. In order to prevent bubble formation in the cell, solutions were injected just prior to data acquisition for measurements after longer time periods.

Results and discussion

We first measured the electrophoretic mobility of the bare latex [surfactant-free AMF latex] as a function of latex concentration going up to 1% wt. The values obtained were essentially constant with latex concentration in water, indicating no important latex–latex interactions in the range of concentrations of the dispersions used. The average electrophoretic mobility value was -4.34 μm cm V^{-1} s^{-1}, which is consistent with the polymerization process.

Upon addition of ALS, the latex particles appeared to be more stabilized, as evidenced by a higher negative value of mobility, averaging -5.10 μm cm V^{-1} s^{-1}. Adsorption of the anionic surfactant at the AMF–water interface confers a more negative surface charge density to the polymers, hence the shift in mobility towards lower values compared to the surfactant-free particles.

Coalescent addition to the bare AMF latex caused little variation in the electrophoretic mobility value of the AMF after 42 h of preparation, as the recordings were in the range of the surfactant-free latex to within ±0.15 μm cm V^{-1} s^{-1}. The latter is considered as the experimental error. Thus, there is no indication of any significant plasticization effect releasing supplemental chain segments or ionic groups at the AMF–water interface.

In a second step, the influence of coalescent addition on the ALS–AMF interface was monitored as a function of time through their electrophoretic properties. Results are presented for each coalescent in Figs. 1, 2, 3, and 4.

For three of the coalescents (DGB, DPM, and TEX) the particle mobility spectrum was observed to be essentially unchanged for the first 3 h. However, we notice that at longer times a weak secondary peak appears in the −1 to −2 μm cm V^{-1} s^{-1} region, and the (AMF + ALS) peak also shifts to less negative values, intermediate between those of the t = 0 (AMF + ALS) and the bare AMF (surfactant-free) latex. The long time main peak mobility values are −4.72 μm cm V^{-1} s^{-1} and −4.53 μm cm V^{-1} s^{-1} for the DPM and DGB systems, respectively. A similar trend is also observed in the case of TEX after 98 h, but in this case, the secondary peak is much larger in size, nearly the same size as the original peak, with a maximum at about −0.94 μm cm V^{-1} s^{-1}. The electrophoretic mobility of the main latex peak shifts to a value even less negative than that of the bare AMF (−3.96 μm cm V^{-1} s^{-1}), indicating a destabilized latex.

As shown in Fig. 4, when EGB is added to the AMF + ALS system, a second peak of appreciable size develops rapidly, within the first 3 h. The 77-h curve shows that this peak decreases in intensity with time, but without disappearing completely. At the same time there is a gradual shift in mobility of the AMF peak to less negative values. At 77 h the main peak is centered at −4.70 μm cm V^{-1} s^{-1}, and the distribution again shows a destabilization effect for the system containing EGB, relative to the original ALS-stabilized latex.

In light of the work by Seebergh and Berg [12], we cannot interpret our results through counterion displacement and change in medium dielectric constant

Fig. 1 Electrophoretic behavior of an AMF + ALS latex in presence of DPM at 25 °C

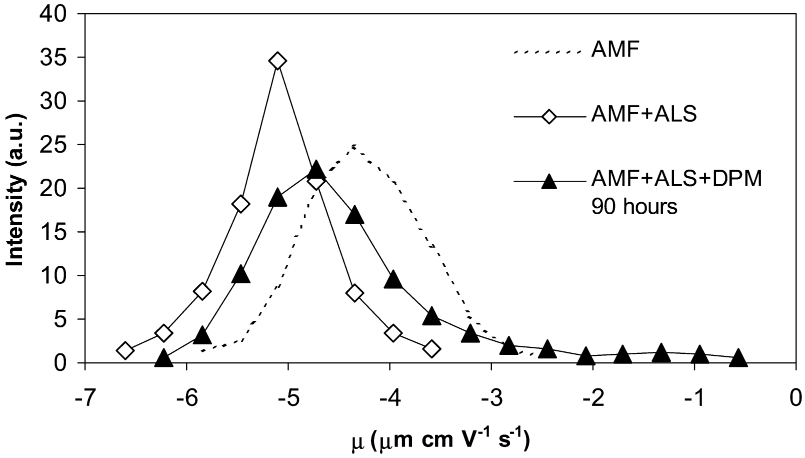


Fig. 2 Electrophoretic behavior of an AMF + ALS latex in presence of DGB at 25 °C

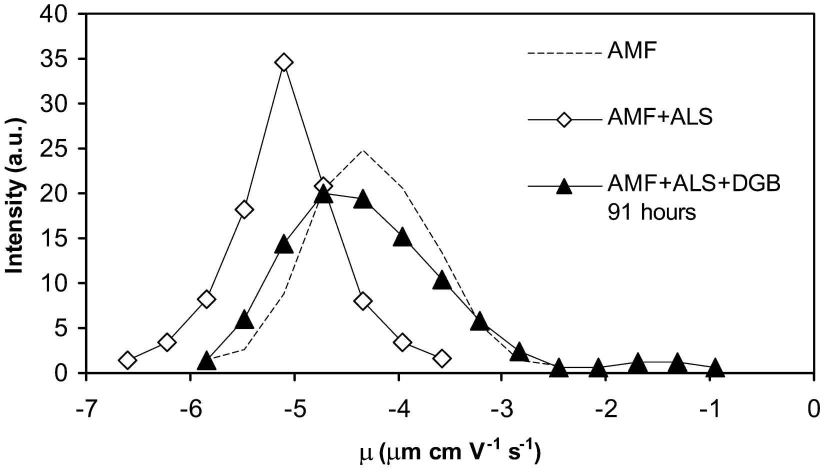


Fig. 3 Electrophoretic behavior of an AMF + ALS latex in presence of TEX at 25 °C

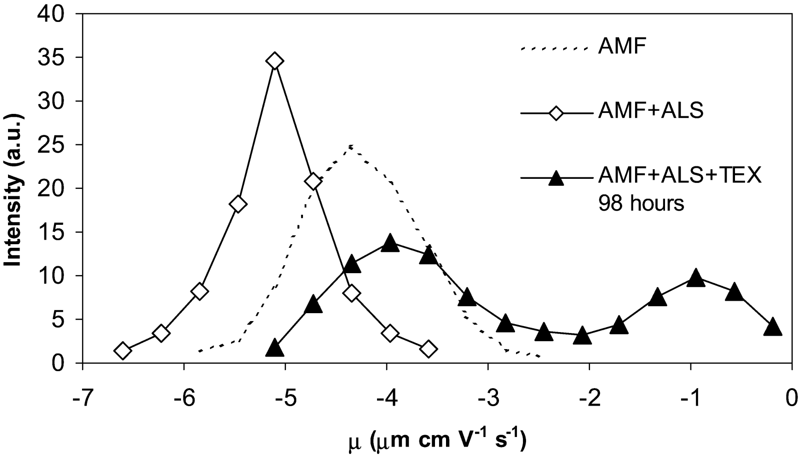
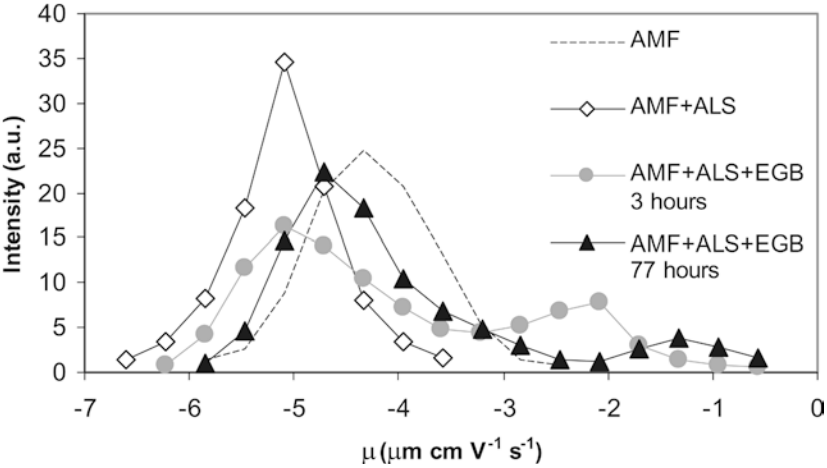


Fig. 4 Electrophoretic behavior of an AMF + ALS latex in presence of EGB at 25 °C



since this work was done in an electrolyte-free medium, all concentrations were held constant and, with exception of EGB, the solvents studied are not as water-soluble as 1-propanol.

It is well known that the addition of solvent to a latex changes the equilibrium between species, as the solvent often partitions between the water phase, latex particles, and solvent droplets. This new equilibrium usually induces a redistribution of surfactants among the different phases. We therefore suggest that the mechanism for the changes in electrophoretic mobility involves surfactant partitioning between the latex particle surface, the aqueous continuous phase, newly formed mixed surfactant micelles (particularly in the case of EGB [18, 19, 20]) and the surface of coalescent droplets (or, especially at long times, droplets of low solubility coalescent impurities, particularly in the case of TEX). The loss of ALS surfactant from the AMF particle surface would account for the observed shift in the particle's zeta potential (which is proportional to mobility) to higher values. In order to account for the observation that the electrophoretic mobility of the [AMF + ALS + TEX] system is lower in mobility than the surfactant-free latex, we suggest that the ALS surfactant that is stripped from the polymer surface increases the ionic strength of the medium, affecting the particle's electrical double layer and hence reducing the mobility of the resulting particles. Solvent partitioning in the particle also depends on the particle composition variation from the surface to the core. In this regard, if AMF particle composition is not homogeneous—and that a gradient between the acrylic-rich region of the surface and the PVDF-rich core exists—it could affect the rate and the amount of solvent that is absorbed.

We further suggest that this mechanism is also involved in the "coalescent shock" or "emulsion shock" phenomenon that is sometimes observed when formulating latex paints. A recent study by the Toronto Society for Coatings Technology [11] notes that little has been published on this relatively common phenomenon, which they connect with microflocculation. The study identified some formulation variables that had an effect on the microflocculation of a test paint formulation. In particular, a blend of hydrophobic coalescents gave more microflocculation than a blend of hydrophilic and hydrophobic coalescent, while the addition of a nonionic block copolymer stabilizer reduced the amount of microflocculation. These results can be easily understood in light of a mechanism whereby the addition of coalescents destabilizes a latex, by means of pulling adsorbed surfactants from the latex particle surface.

The electrophoretic mobility effects of coalescents in dilute latex might have been anticipated, based on the reports of migration of surfactants reported in polymer films dried from latex. Juhué et al. [21] have demonstrated that exudation of surfactant post-added PBMA films increases with increasing levels of coalescing aid. Also, different effects on the displacement of the surfactants are expected for different coalescents, since the coalescents themselves do not partition equally between the water and polymer interface in the latex [22]. Depending on their molecular structure and their partitioning coefficients, the coalescents should be expected to influence surfactant–polymer interactions even in waterborne systems.

Conclusions

Measurement of electrophoretic mobility proved to be a very valuable tool in studying the effect of surfactant and coalescent addition to latex stability. We showed that the electrophoretic mobility of the surfactant-free latex is not affected by the presence of coalescents (TEX, DGB, DPM, and EGB) either at short or long times, while the surfactant-stabilized AMF latex is affected in a dramatic way by the addition of coalescents. We also showed that addition of coalescent to latex pre-stabilized with ALS surfactant generates a secondary colloidal population, with lower electrophoretic mobility than the latex particles themselves. We also observed that the effect of coalescent addition varies with the nature of the coalescent. For the case of EGB, this second population is formed immediately after the coalescent addition, but it substantially disappears after several days. For the other coalescents studied (TEX, DGB, and DPM), the second population is formed only after some hours, and can be clearly seen in the mobility spectra more than 90 h after the coalescent addition. In the case of DGB and DPM, this secondary mobility peak appears as a small peak on the side of the main peak. At the same time, a shift of the latex electrophoretic mobility peak toward higher values occurs, indicating a somewhat destabilized dispersion. In the case of TEX, the latex was more stable as exemplified by the shift of the main particle peak towards lower values, (with values even lower than the bare AMF particles) and the amplitude of the secondary peak was much larger. The secondary peak is hypothesized to be some kind of surfactant–coalescent adduct or floc structure that has the net effect of redistributing surfactant away from the surface of the latex particles. This would tend to destabilize the latex particle dispersion, which could result in microflocculation in real-life latex formulations. These results show that any mechanisms studying paint flocculation should take into account the way that coalescing aids affect the partitioning of surfactants between the polymer interface and the water phase. Parallel to the work of the Toronto Society, we identify that largely hydrophobic or hydrophilic coalescing aids significantly destabilize the dispersion, whereas for the medium range hydrophobicity solvents, the destabilizing effect is felt to a lesser extent.

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