Using Dispersion/Flocculation Phase Diagrams to Visualize Interactions Of Associative Polymers, Latexes, And Surfactants

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The colloidal interactions of associative polymers and latexes in the presence of surfactant are complex. This is because, in addition to good particle dispersion, both brid-ging and depletion flocculation can occur. Therefore, we have developed phase diagrams to help visualize these interactions. The various phases have a significant effect on coatings and applications properties. Examples of phase diagrams are presented for a model HEUR nonionic associative polymer and latexes in the presence of sodium dodecylsulfate. The major variables affecting phase behavior were found to be associative polymer concentration, latex particle size, latex surface hydrophobicity, and electrolyte, cosolvent, and surfactant concentrations.

INTRODUCTION

Background

Over the past two decades, associative polymers (also known as associative thickeners and rheology modifiers) have been a very useful tool to improve applications properties of latex paints.[1] They provide good in-can appearance, thickening efficiency, and spatter resistance, in addition to excellent flow and leveling, hiding, uniform film formation, and gloss development. The two major types of associative thickeners used in coatings are nonionic and anionic. The most common nonionic associative thickeners have a polyoxyethylene (POE) backbone with terminal hydrophobic groups and are known as Hydrophobically-modified Ethoxylated Urethanes (HEUR) thickeners. The most common anionic associative thickeners are based on a polyelectrolyte backbone with pendant hydrophobes and are known as Hydrophobically-modified Alkali-Swellable Emulsion (HASE) thickeners. This article will discuss only an HEUR system, although the same principles apply to the HASE systems. HASE systems will be discussed in a future publication.

The use of associative thickeners has necessitated a significant amount of reformulation due to the complicated interactions they undergo with practically every coatings formulation component. Traditional nonassociative thickeners such as hydroxyethylcellulose (HEC) and anionic alkali soluble emulsions (ASE) interact very little with the formulation components and thicken coatings by virtue of their molecular volume and particle flocculation characteristics. In contrast, associative polymers, by virtue of their hydrophobic functionality, interact with latex particles, pigments, fillers, surfactants, and cosolvents. These interactions can lead to good particle dispersion, which produces superior rheological, optical, and barrier properties. Under some conditions, the hydrophobic interactions can be mitigated to the point where particle flocculation occurs. This leads to degraded properties due to poor latex and pigment dispersion. In order to help visualize the complicated interactions in these systems, we developed dispersion/flocculation phase diagrams[2] for both latex and

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pigment systems. All particles follow the same rules of dispersion in associative thickener systems, but the subject for pigments is complicated by the presence of dispersants of variable composition and concentration. Therefore, the phase behavior of pigment suspensions containing associative thickener will be discussed in a future publication, while the focus here is solely on latex systems.

Latex Dispersion States

This article discusses the interactions that can occur in a latex containing both associative polymer and surfactant. In its unthickened, unformulated state, a typical latex exists in a well dispersed state wherein the particles undergo Brownian motion. *Figure* 1 is a photomicrograph of such a latex where the majority of particles are too small to see, but the larger gel particles are visible. When the first amount of HEUR is added to the latex, it adsorbs onto the particles, connecting them to produce bridging flocculation.[2-5] There is room for the hydrophobes to adsorb on the particles because surfactant levels in commercial latexes are generally kept low (i.e., well below saturation) so that applications properties are not adversely affected. Bridging flocculation is shown in the micrograph in *Figure* 2. As more HEUR is added, there are sufficient connections to form a uniform network and uniform particle dispersion. This good dispersion, which lacks Brownian motion because it is thickened, is shown in *Figure* 3. Adding additional surfactant will also bring the latex into the good dispersion region. Thus, bridging flocculation can be alleviated by adding additional associative polymer, surfactant, or both to the system. This good dispersion is the desired state for improved coatings properties. As more surfactant is added to this system, the associative polymer is displaced from the particle surfaces and depletion flocculation occurs. This is pictured in *Figure* 4 (bottom) and is the normal state for systems thickened with nonassociative polymers. This poor dispersion can lead to degraded optical and physical properties in the coating. Practical coatings typically have sufficient HEUR polymer and surfactant so that bridging is not a problem, but depletion flocculation can be brought on, for example, by excess surfactant added with a colorant.

Depletion Flocculation

Depletion flocculation is actually an osmotic pressure phenomenon which occurs when nonadsorbed thickener molecules are excluded from the space between particles.[6] It is dependant upon the particle volume solids, particle size, thickener molecular size, and concentration. This osmotic attraction energy is only one of the factors comprising the total interparticle potential energy (V_{tot}) of the system, which in turn determines the dispersion state of the system. The total interparticle potential energy can be expressed as follows:

$$V_{tot} = V_{vdw} + V_{elec} + V_{depl} \tag{1}$$

where V_{vdw} is the van der Waals attractive energy, V_{elec} is the electrical repulsive energy, and V_{depl} is the attractive depletion energy, which is a function of the particle radius, polymer radius, and osmotic pressure (polymer conc. and Mn).

Figure 5 shows the potential energy curves for a well dispersed system and a depletion flocculated system. The effect of depletion flocculation is that the particles cluster close to each other in a shallow (secondary) energy minimum. Mechanical shear will redisperse them, but the flocculated structure will reform quickly. *Figure* 4 is a sequence of photomicrographs showing a depletion flocculated latex immediately after shear (top), 10 seconds after shear (middle), and 20 seconds after shear (bottom). In the top of *Figure* 4, the latex has been mechanically redispersed by applying mechanical energy exceeding the secondary minimum energy. In the middle of *Figure* 4, the flocs are reforming. In the bottom of the figure, the flocs have fully formed, the state the system was in before shearing. This gives some idea of the flocculation rate, but flocculation rate will vary significantly with viscosity. The poor particle dispersion in a depletion flocculated system leads to lower gloss, lower hiding, and poorer film integrity and adhesion. Bridging flocculation is generally a stronger interaction, is more difficult to break up with mechanical energy, and reforms faster than depletion flocculation. Depletion flocculation is more commonly encountered in coatings than bridging flocculation.

Phase Diagrams

In order to visualize the regions of dispersion and flocculation, we developed experimental techniques to generate phase diagrams for systems containing latex, surfactant, and associative polymer. *Figure* 6 is a generalized version of the diagram showing the regions of dispersion and flocculation as previously described. The upper boundary of the bridging region is really a continuum of ever increasing floc sizes until a uniform dispersion is reached. We have defined this upper boundary as the point at which individual flocs are no longer noticeable by microscopic inspection of the samples. The lower depletion flocculation boundary is the critical flocculation concentration (CFC) of the thickener, below which depletion flocculation does not occur. These diagrams will be used to illustrate the effect of latex particle size, composition, cosolvent, and electrolyte on dispersion.

Rheology

Associative polymers produce a different, more favorable, rheology profile than nonassociative thickeners. *Figure* 7 shows viscosity vs. shear rate curves for two coatings formulations having about the same Krebs-Stormer viscosity, but one is thickened with HEUR and the other is thickened with a nonassociative thickener (HEC). Note that the low shear viscosity of the HEUR system is significantly lower than the nonassociative system. This leads to excellent flow and leveling. On the high shear end, the HEUR exhibits higher viscosity, leading to higher film build. The rheology of associative polymer/latex systems is complex[7,8] and is beyond the scope of this article, which concentrates on phase behavior. Suffice it to say that, when associative

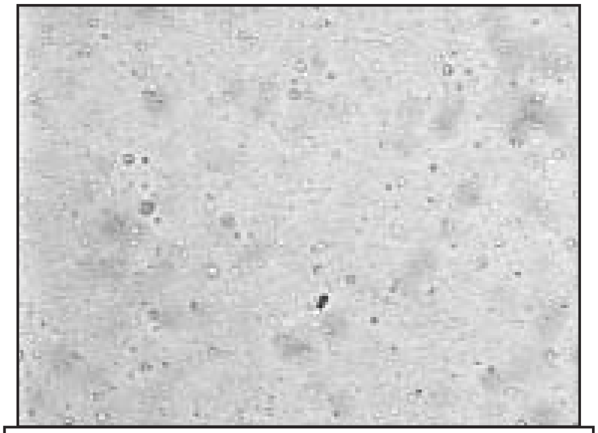

Figure 1—Photomicrograph of an unthickened latex. The primary particles are too small to see, but the larger gel particles are clearly visible. The particles are undergoing Brownian motion.

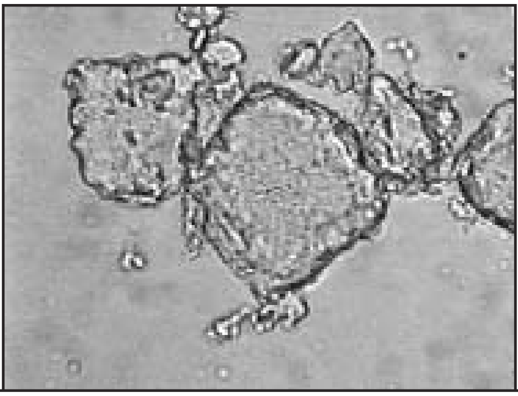

Figure 2—Photomicrograph of the latex from Figure 1 containing a small amount of HEUR thickener. Because there is not enough HEUR to cover at least 50% of the surface, bridging flocculation occurs. These flocs are large and very difficult to shear apart.

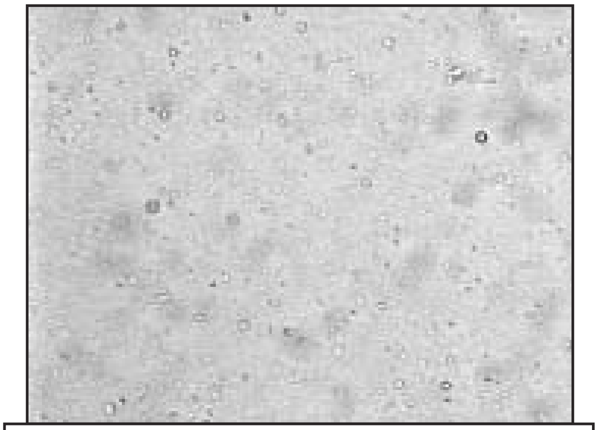

Figure 3—Photomicrograph of the latex from Figure 1 containing enough HEUR to yield a good, uniform dispersion. The particles are not undergoing Brownian motion. This is the desired dispersion state for superior coatings properties.

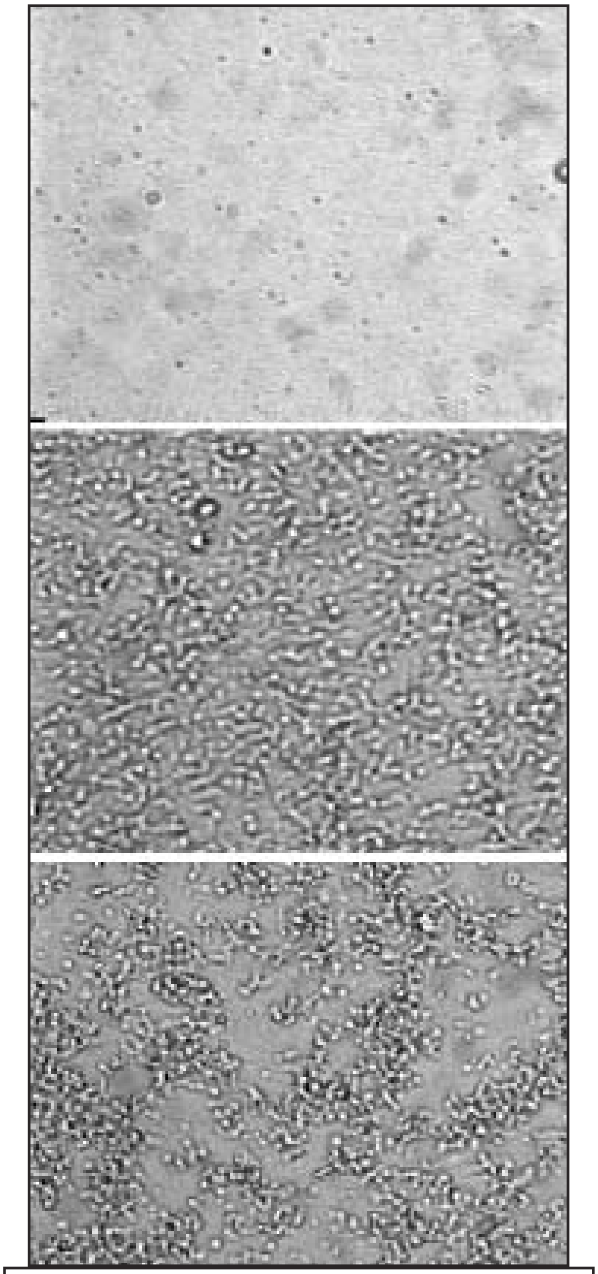

Figure 4—A series of photomicrographs showing depletion flocculation caused by the addition of excess SDS surfactant to the latex/HEUR system in Figure 3. The first micrograph (top) shows the flocculated latex immediately after being sheared. The second micrograph (middle) shows the sample 10 sec later, as the flocs begin to form. The third micrograph (bottom) shows the sample 20 sec after shear, with the flocs fully formed. This is the "at rest" state of a depletion flocculated latex and is typical of systems thickened with nonassociative polymers.

systems become flocculated, they revert to nonassociative rheology. In order to optimize the coating rheology, it is now common practice to utilize a combination of thickeners in the same formulation.

EXPERIMENTAL

Materials

The following materials were used to determine the latex phase behavior:

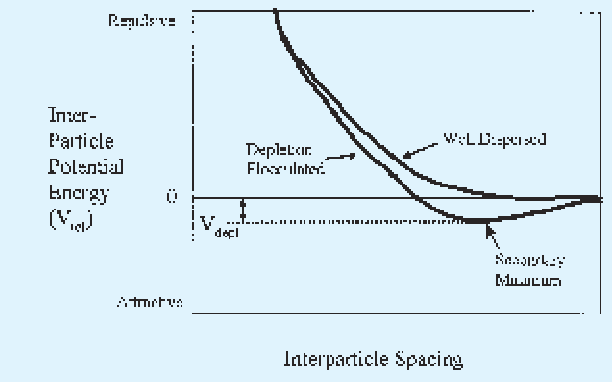

Figure 5—Total potential energy curves for latex particles that are well dispersed and that are depletion flocculated. The flocculated particles reside in a secondary energy minimum well whose depth is equal to the depletion energy. Mechanical energy such as shear can remove the particles from the minimum, but they quickly return when the shearing is stopped (see Figure 4).

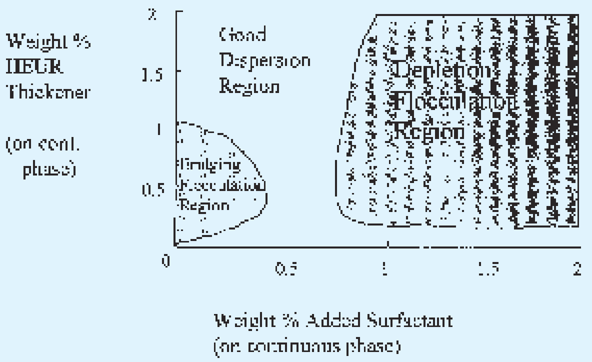

Figure 6—Idealized phase diagram showing the three major regions which result from interaction of latex particles with HEUR thickener and surfactant. The latex can be removed from the bridging region by the addition of HEUR and/or surfactant. The upper portion of the good dispersion region provides superior coatings properties and sufficient viscosity for application. The system enters the depletion flocculation region as extra surfactant is added.

- Model associative polymer—HEUR-type polyoxyethylene backbone with terminal C12 hydrophobes (average molecular weight of 50,000)
- Nonassociative polymer—Hydroxyethylcellulose (HEC) of 600,000 molecular weight
- Latexes—50 BA/50 MMA, some BA/Sty at various particle sizes 140 – 600 nm in diameter. All latexes contain 1% MAA and 0.05-0.10% sodium dodecylbenzene sulfonate (SDBS) on total monomer weight
- Added surfactant—Sodium dodecyl sulfate (SDS) and Triton® X-100
- Electrolyte—NaCl
- Cosolvents—methyl carbitol and butyl carbitol
- Latex Solids—25% (by volume)

Note that concentrations of additives are expressed as weight % of the continuous phase and that the SDBS surfactant levels from the latex synthesis are very low based on the continuous phase (0.02-0.03%) and are very low compared to the added SDS in the phase diagrams.

Determination of Particle Dispersion

Mixtures of latex, HEUR, and surfactant were prepared in clear glass containers at 25% polymer solids by volume. Particle dispersion was assessed by both visual inspection and microscopy. The bridging flocculation region was confirmed by the fact that higher levels of surfactant and/or HEUR eliminated the flocculation. Depletion flocculation could be confirmed by the fact that dilution of the sample with water to below the critical flocculation concentration yielded a well dispersed system. An average of 30-40 samples were prepared for each system to define the dispersion and flocculation regions with some precision. The most difficult systems were those containing high levels of HEUR and surfactant because the high viscosity led to slow flocculation kinetics and mixing problems. Latexes of 300 nm in diameter were chosen as a "typical" size for evaluating the variables of latex surface hydrophobicity and composition, added electrolyte, and added cosolvent.

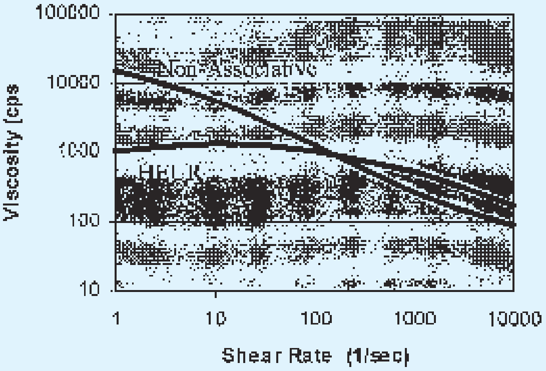

Figure 7—Rheology curves for typical HEUR and nonassociative thickened latex having similar Krebs-Stormer viscosities. Note the lower low shear viscosity and the higher high shear viscosity of the HEUR system compared to the nonassociative system.

RESULTS AND DISCUSSION

Nonassociative Thickeners

As a control, the phase diagram for a typical nonassociative thickener, hydroxyethyl cellulose (HEC), was generated. A 300 nm BA/MMA latex thickened with HEC was chosen for this purpose. *Figure* 8 is the resulting phase diagram. Note that the latex was depletion flocculated at all but the very lowest thickener concentration and that SDS had no effect on the dispersion. This is in sharp contrast to what is observed for the latexes with HEUR thickener.

Associative Thickeners

Particle Size Effects on BA/MMA Latexes: One of the latex properties that is commonly varied is particle size. Model BA/MMA latexes of 300, 600, and 140 nm particle diameter were studied in the presence of the HEUR and SDS. The resulting phase diagrams are shown in *Figures* 9, 10, and 11, respectively. These diagrams represent the baseline behavior to which other systems can be compared. The major effect of latex particle size is that the smaller the particle size, the larger the good dispersion region. This is due to the increased surface area of the latex available for interaction with the HEUR and SDS. In addition, the CFC in the depletion region increases with decreasing latex size in accordance with depletion theory,[6] which states, that, at a given volume solids, the smaller the latex the smaller the volume from which the soluble polymer is excluded. This effectively lowers the concentration of the water soluble polymer in the nonexcluded portion of the continuous phase, thus lowering osmotic pressure. The CFC of HEURs is lower than expected due to the fact that SDS associates with the POE backbone. This results in a pseudo-polyelectrolyte structure with expanded molecular volume.

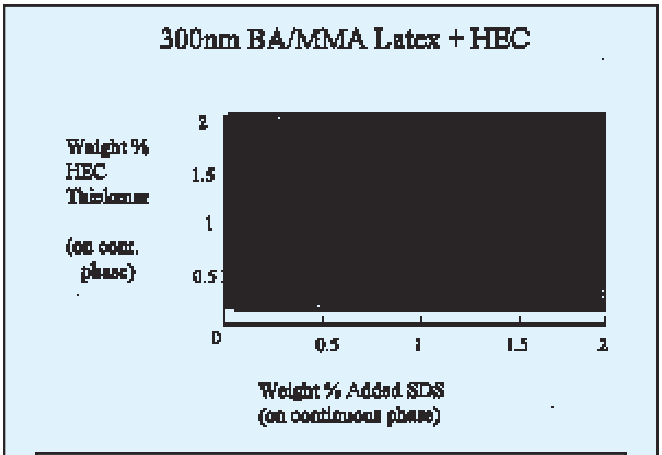

Figure 8—Phase diagram of a 300 nm BA/MMA latex thickened with HEC, a nonassociative thickener. The latex is depletion flocculated at all but the very lowest thickener concentrations (i.e., those below the critical flocculation concentration). SDS has no effect on the phase behavior. This diagram is typical of nonassociative systems.

Electrolyte Effects: Electrolytes have multiple effects on HEUR/latex systems. They tend to increase the strength of the hydrophobic interactions by a salting out effect on both the HEUR and the surfactant. In addition, they decrease the hydrodynamic volume of both the latex and the soluble polymer, especially the pseudo-polyelectrolyte structure formed by SDS and the POE chains. This has the effect of increasing the area of good dispersion. *Figure* 12 illustrates the effect for the 300 nm BA/MMA latex with and without 1% NaCl in the continuous phase. Note that both the bridging and depletion flocculation regions have decreased in size, leaving a larger area of good dispersion.

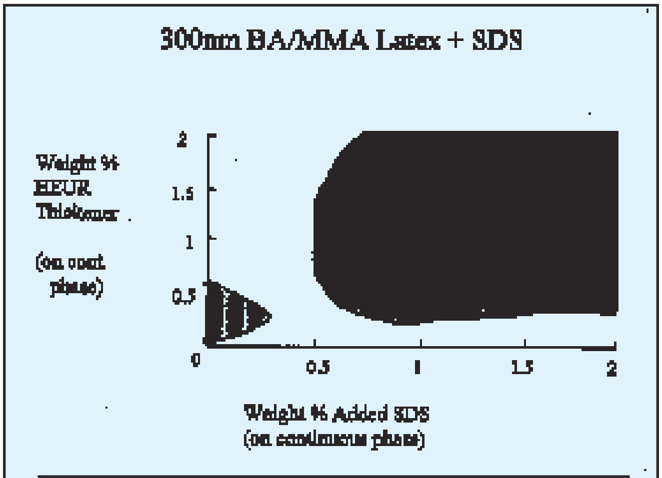

Figure 9—Phase diagram of a 300 nm BA/MMA latex thickened with HEUR. Note the bridging, good dispersion, and depletion flocculation regions from left to right. This is our "standard" phase diagram to which others will be compared.

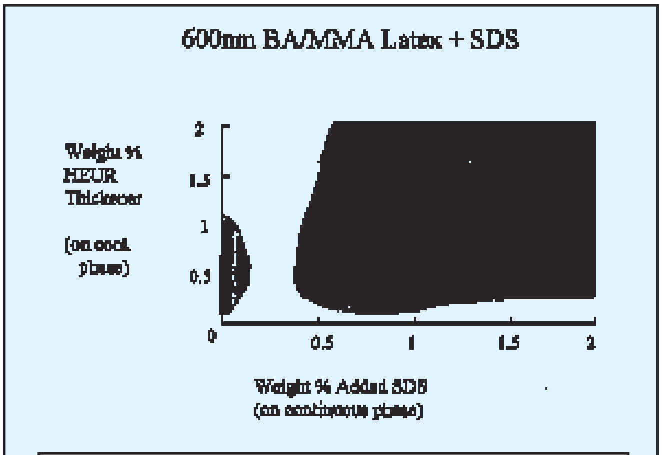

Figure 10—Phase diagram of a 600 nm BA/MMA latex thickened with HEUR. The larger particle size latex, having less surface area, leads to a smaller region of good dispersion. The larger particle size also yields a lower critical flocculation concentration (CFC) in the depletion region.

HYDROPHILIC LATEX SURFACE: When the latex surface is made more hydrophilic, as when carboxylic acid-based monomers are used in the polymerization, the number of hydrophobic sites available for the surfactant and HEUR hydrophobes is reduced. This leads to a smaller bridging region and decreased region of good dispersion due to the small amount of surfactant needed to saturate the latex surface and to displace the HEUR. *Figure* 13 shows such a phase diagram for a 300 nm BA/MMA latex having a high concentration of surface acid (4% MAA based on total monomer weight).

HYDROPHOBIC LATEX SURFACE: When the latex surface is made more hydrophobic, interactions with the HEUR molecules are increased. BA/Sty latexes were prepared having 300, 600, and 150 nm diameters. The phase diagrams for these latexes are shown in *Figures* 14, 15, and 16, respectively. As with the BA/MMA system, the smaller the particle size, the larger the region of good dispersion. At the same particle size, the more hydrophobic latex tends to have a larger bridging region, but also a larger good dispersion region.

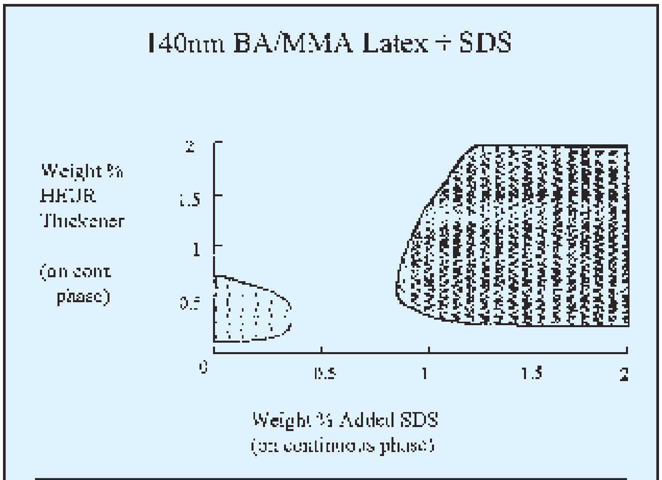

Figure 11—Phase diagram of a 140 nm BA/MMA latex thickened with HEUR. The smaller particle size latex, having more surface area, leads to a larger region of good dispersion. The smaller particle size also yields a higher critical flocculation concentration (CFC) in the depletion region.

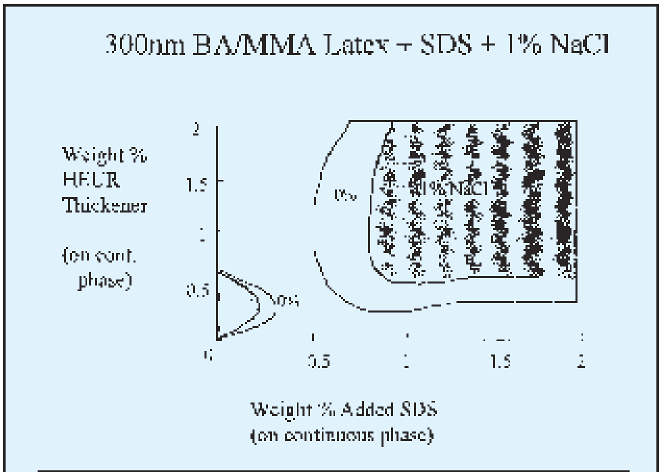

Figure 12—Phase diagram of a 300 nm BA/MMA latex with and without 1% NaCl. The added electrolyte has the effect of increasing the good dispersion region by shrinking both the bridging and depletion regions. This is caused by the increased efficacy of the hydrophobes on both HEUR and SDS to adsorb onto the latex.

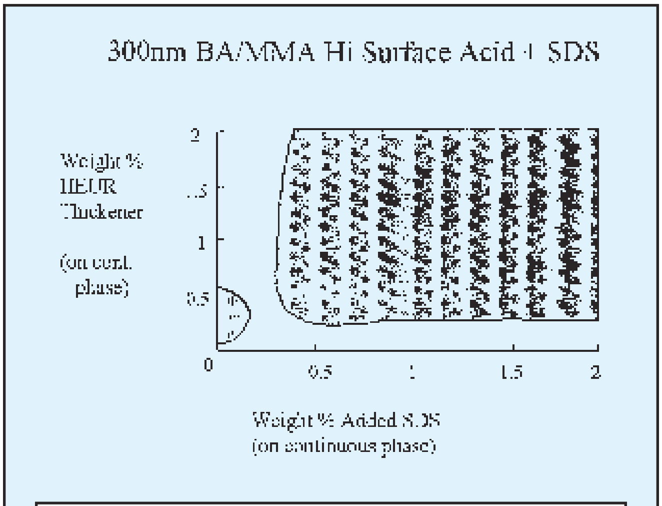

Figure 13—Phase diagram of a 300 nm BA/MMA latex having a high concentration of surface acid. This makes the surface very hydrophilic and significantly reduces the area which hydrophobes can absorb. The consequence is a much reduced region of good dispersion.

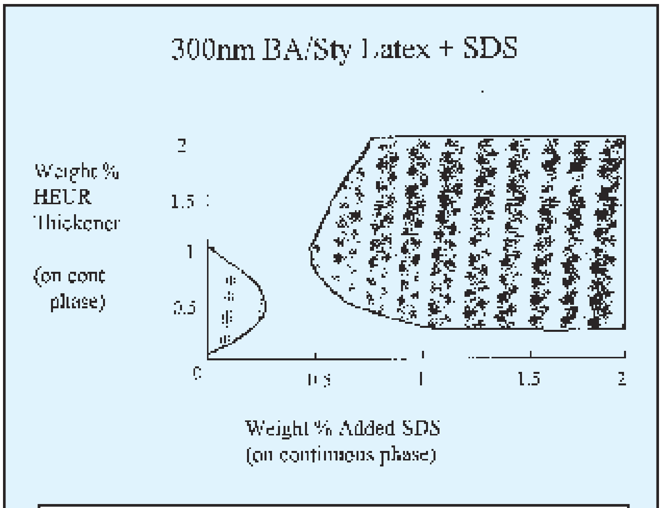

Figure 14—Phase diagram of a 300 nm BA/Sty latex thickened with HEUR. Due to the increased hydrophobicity, the bridging and good dispersion regions are larger than those for the standard 300 nm BA/MMA latex.

Cosolvent Effects: One way to mediate and control the strength of the associations in an associative polymer system is to formulate with water miscible cosolvents. Such cosolvents disrupt the water structure and associative thickener network. In addition, they reduce the adsorption of the HEUR molecules on the latex surface and provide more places in the total system for the SDS to interact, thus mediating the effects of the SDS. As one might expect, the more hydrophobic the cosolvent, the larger the effect it has on the dispersion characteristics of the system. *Figure* 17 shows the progressive effects of using methyl carbitol and butyl carbitol in the system at a typical level of 9% by weight in the continuous phase. Butyl carbitol, because it is more surfactant-like than methyl carbitol, yields larger effects, even to the point of eliminating the bridging flocculation altogether in this example while increasing the good dispersion region. Adsorption experiments suggest that this level of butyl carbitol reduces HEUR adsorption on the latex by 50%. Cosolvents have a significant effect on rheology, generally reducing overall viscosity.

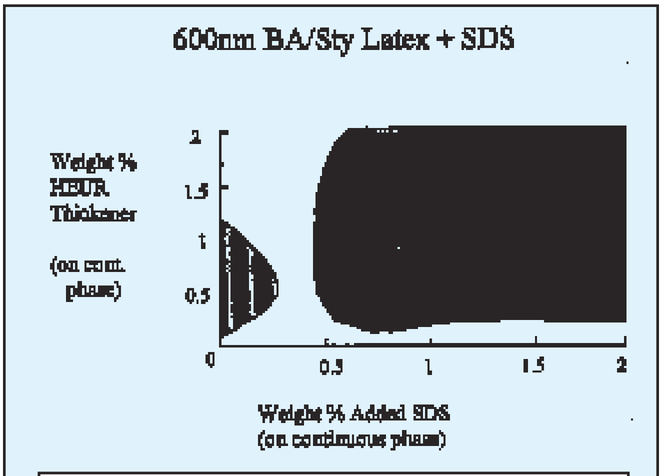

Figure 15—Phase diagram of a 600 nm BA/Sty latex thickened with HEUR. As with the BA/MMA system, the larger particle size latex, having less surface area, leads to a smaller region of good dispersion. The larger particle size also yields a lower critical flocculation concentration (CFC) in the depletion region.

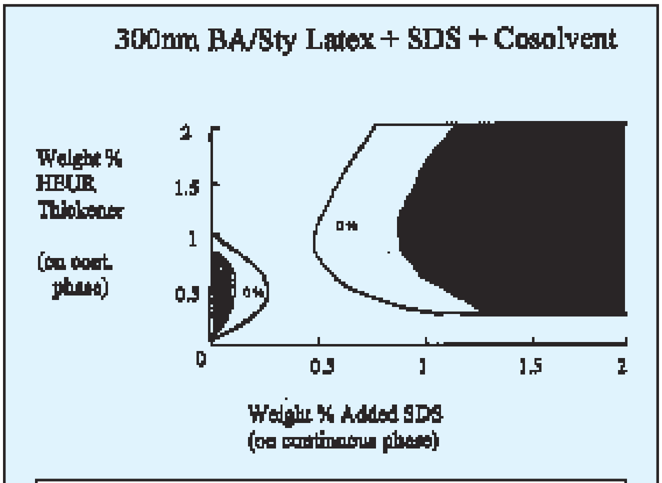

Figure 17—Phase diagram of a 300 nm BA/Sty latex with added cosolvent. The cosolvents have the effect of increasing the good dispersion region by mediating the hydrophobic interactions. The more hydrophobic (or surfactant-like) the cosolvent, the larger the effect. Thus, butyl carbitol increases the good dispersion region, even to the point of eliminating the bridging region.

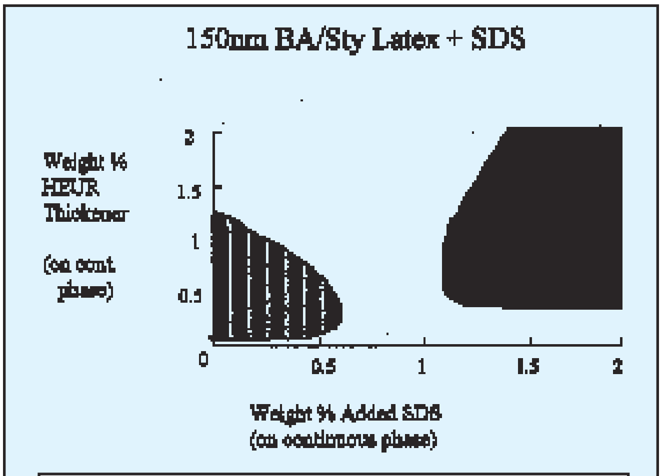

Figure 16—Phase diagram of a 150 nm BA/Sty latex thickened with HEUR. As with the BA/MMA system, the smaller particle size latex, having more surface area, leads to a larger region of good dispersion. The smaller particle size also yields a higher critical flocculation concentration (CFC) in the depletion region. Note the very large bridging region due to the increased area and hydrophobicity.

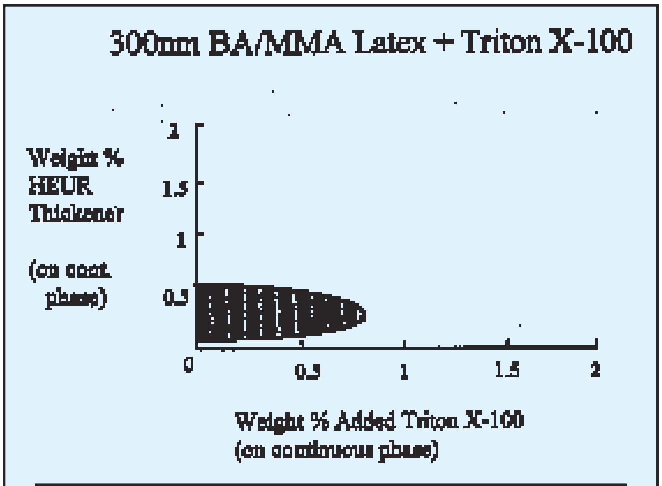

Figure 18—Phase diagram of a 300 nm BA/MMA latex to which a nonionic surfactant, rather than SDS has been added. The bridging region remains, but the depletion region is absent, presumably because of the compatibility of the POE chains on the surfactant and the HEUR.

NONIONIC SURFACTANT: A nonionic surfactant with a POE hydrophilic chain should be compatible with the HEUR thickener. Triton X-100 is an example of a low HLB surfactant of this type. When we added this surfactant to the standard 300 nm BA/MMA latex, we observed the usual bridging flocculation region, but not the depletion region, within the 2% weight limit of these experiments. This is shown in *Figure* 18. Triton X-100 does not appear to be very efficient at displacing HEUR from the latex surface. Also, Triton X-100 is much less efficient than SDS at eliminating bridging flocculation due to its higher molecular weight.

CONCLUSIONS

The following conclusions can be drawn based on the structure of the phase diagrams generated in the work presented here:

(1) Associative polymers, in combination with latex particles and surfactant, exhibit complex dispersion behavior which depend on the concentration of each component plus latex particle size and surface composition.

(2) Latex particle size, electrolyte concentration, and cosolvent type and concentration have the most significant effect on the relative sizes of the well dispersed and flocculated regions.

(3) Good dispersion and both bridging and depletion flocculation of the latex are observed in HEUR systems if one begins at low initial surfactant levels. In contrast, latexes thickened with nonassociative polymers exist only in the depletion flocculated state, except at very low thickener concentrations.

(4) Systems with POE nonionic surfactant have a bridging, but no depletion flocculation region within the concentrations explored in this work.

(5) Dispersion/flocculation phase diagrams are a unique way to visualize the colloidal dispersion behavior of latex particles with associative polymers and surfactants.

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