Surfactant and Electrolyte Effects on Latex Depletion Flocculation by Thickeners

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Summary: Polymer thickeners can induce good dispersion, bridging, or depletion flocculation of latexes depending on the polymer structure and concentration. Unlike non-associative polymers, associative polymers have the ability to create a good latex dispersion. However, when the associative interactions are destroyed, depletion flocculation of the latex can result. This happens when an excess of ionic surfactant is added to the system. In addition, the surfactant may associate with the thickener backbone, thus modifying the molecular volume of the polymer thickener. This paper explores the effect of anionic surfactant and electrolyte on the molecular volume of both associative and non-associative thickeners. Both HEUR and HASE structures are included. For HEUR thickeners, formation of a pseudo-polyelectrolyte through the association of anionic surfactant with the polyethylene oxide backbone is confirmed. Further, the ability of the thickener to depletion flocculate latexes as a function of surfactant and electrolyte is explored. Experimental critical flocculation concentrations (CFC) are compared to values expected based on molecular volume and potential energy calculations. A good correlation is found between molecular volume and CFC for a wide range of thickener compositions.

Keywords: association; colloids; hydrophilic polymers; latices; surfactants

Introduction

Associative thickeners are now commonly used in aqueous latex-based coatings to impart superior rheological, application, and optical properties to coatings as compared to their non-associative thickener counterparts.[1] This is accomplished by forming an association network between the thickeners and the particles (latex and pigment) in a coatings formulation.[2–5] The good particle dispersion in associative systems is in contrast to the depletion flocculated state normally occurring in non-associative systems. Associative networks can be strengthened by addition of electrolyte and can be weakened, and ultimately destroyed, by addition of excess ionic surfactant. When the association is destroyed, associative polymers revert to non-associative behavior due to depletion flocculation of the particles by the thickener.[4,5]

The ability of a soluble polymer thickener to induce depletion flocculation is a function of its molecular size and concentration.[6–10] A complicating factor is that anionic surfactants, in addition to destroying hydrophobic networks through micellar interactions, can associate with certain polymer backbones such as polyoxyethylene.[11–12] The resulting pseudo-polyelectrolyte has an expanded conformation that is highly dependent on electrolyte concentration, just as the true polyelectrolyte thickener size is dependent on electrolyte concentration. This paper explores the effect of surfactants and electrolytes on the molecular size of several types of polymers including HEUR and HASE associative thickeners and hydroxyethyl cellulose (HEC), polyoxyethylene (pEO), and polyacrylamide (pAM) non-associative thickeners. HEURs are Hydrophobically-modified Ethoxylated Urethanes synthesized by

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step-growth polymerization of a diisocyanate with 6,000–8,000 molecular weight polyoxyethylene diol, capped with C_8–C_{16} alcohols. HASEs are Hydrophobically-modified Alkali Swellable Emulsions synthesized by copolymerization of methacrylic acid and ethyl acrylate, with pendant hydrophobes attached polyoxyethylene chains. In addition to molecular size determination, the depletion flocculation behavior of acrylic latexes in the presence of these thickeners is measured (i.e., critical flocculation concentration) and compared to results from interparticle potential energy calculations including depletion flocculation energy based on the molecular size data.

Experimental Part

The molecular size of several selected thickeners and their ability to depletion flocculate a model acrylic latex were investigated in this study. The following materials were used for the experiments:

Model Associative Polymers

HEUR-type polyoxyethylene backbone with terminal $C_{12}H_{25}$ hydrophobes and also a nonassociative version with terminal Cellosolve synthesized at Rohm and Haas by the method given in U.S. Patent 4,079,028. HASE-type thickeners with MAA/EA copolymer backbone and pendant $C_{12}H_{25}$ synthesized at Rohm and Haas. All polymers were unfractionated.

Nonassociative Polymers

hydroxyethyl cellulose (HEC), polyoxyethylene (pEO), and polyacrylamide (pAM) and were commercial samples used ‘‘as is’’ without fractionation.

Model Latex

BA/MMA = 50/50 copolymer with particle size of 600 nm diameter and 0 °C glass transition temperature. Latex was synthesized by seeded emulsion polymerization at Rohm and Haas using 1% MAA and 0.05–0.10% sodium dodecylbenzenesulfonate (SDBS) based on total monomer weight. Zeta potential determined using Malvern Zetasizer.

Surfactants

commercial anionic surfactant sodium dodecyl sulfate (SDS) and nonionic surfactant Triton® X-405 (octylphenol ethoxylate 40 (OP $(EO)_{40}$)).

Electrolyte

commercial sodium chloride (NaCl).

Molecular size of the various polymer thickeners was determined by first measuring intrinsic viscosity of the polymer solutions with and without surfactants and electrolyte by capillary viscometry. Intrinsic viscosity determination was done at 25 °C using a No.100 Cannon-Ubbelhode dilution viscometer. The viscosity average molecular weight (M_v) was calculated from the relation given by Brown[13] and the number average molecular weight (M_n) was derived from that.[14] The polymer diameter was expressed as twice the RMS radius of gyration.[7]

Aqueous mixtures of latex and thickener were prepared in clear glass containers at 0.25 volume fraction polymer latex and allowed to equilibrate for at least 60 hours before evaluation. Latex dispersion was assessed by both visual inspection and microscopy. Samples that were severely flocculated displayed visual phase separation. All samples were inspected by light microscopy at 400X magnification. At this magnification the individual latex particles are not visible, but flocculated particles are easily visible as aggregates and phase-separated regions. When flocculation was detected, extra samples with small adjustments of polymer concentration were prepared to determine the critical flocculation concentration (CFC) as precisely as possible. Depletion flocculation (as opposed to bridging flocculation) could be confirmed by the fact that dilution of the sample with water to below the CFC yielded a well dispersed system. CFC is expressed as micromolar concentration in the continuous phase, whereas additive

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Table 1.
Thickener intrinsic viscosity and derived Mv and Mn.

Thickener	Intrinsic Viscosity (dl/g)	M_v	M_n
HEUR	0.62	72,650	37,256
HEUR without hydrophobes	0.71	85,710	43,954
Polyoxyethylene	1.10	146,180	74,964
HASE	15.85	500,000	256,410
Hydroxyethyl cellulose I	1.59	71,600	36,718
Hydroxyethyl cellulose II	2.55	124,300	63,744
Polyacrylamide	0.58	90,000	46,154

concentrations (SDS, NaCl) are expressed as weight % in the continuous phase.

Results and Discussion

Intrinsic viscosity measurements were used to characterize the polymeric thickeners and then molecular weights were derived from the viscosity data. Table 1 lists the results for HEUR, HASE, pEO, HEC and pAM thickeners in water only. The molecular size and association of HEUR thickeners has been studied by neutron and X-ray scattering studies, but that work utilized polymers of much lower molecular weight and did not address electrolyte and surfactant effects.[15,16]

In order to determine the effect of surfactants and electrolyte on molecular size of these polymeric thickeners, intrinsic viscosity was measured in the presence of the anionic surfactant SDS, the nonionic surfactant Triton® X-405, and the electrolyte NaCl. Molecular diameter was calculated from the intrinsic viscosity data. Table 2 shows the results for the HEUR, HEUR without terminal hydrophobes, polyoxyethylene, and HASE thickener. For HEUR thickener, SDS forms a pseudo-polyelectrolyte with the backbone, resulting in a more than 50% increase in molecular diameter compared to the diameter in pure water. NaCl was able to decrease significantly the size of the SDS-HEUR complex. Nonionic surfactant had little effect on the HEUR size. For the purposes of comparison, a difference of 5% in molecular diameter is significant. For example, there is no significant difference

Table 2.
Molecular diameter of associative and related polymers under various conditions.

Polymer	% Triton® X-405	% SDS	% NaCl	Molecular Diameter (nm)
HEUR	0	0	0	18.9
HEUR	0.6	0	0	19.2
HEUR	0	0.25	0	24.1
HEUR	0	0.50	0	29.1
HEUR	0	1.00	0	29.5
HEUR	0	1.00	1.00	22.2
HEUR no hydrophobes	0	0	0	20.9
HEUR no hydrophobes	0	0.60	0	20.9
HEUR no hydrophobes	0	1.00	0	31.8
HEUR no hydrophobes	0	1.00	1.00	24.5
HEUR no hydrophobes	0.60	0	1.00	21.3
pEO	0	0	0	28.9
pEO	0.60	0	0	29.2
pEO	0	1.00	0	43.6
pEO	0	1.00	1.00	33,7
HASE	0	0	0	127.3
HASE	0.60	0	0	128.0
HASE	0	0.10	0	100.0
HASE	0	0	0.15	80.8
HASE	0	0	1.00	56.6

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Table 3.
Molecular diameters of non-associative thickeners in different solvents.

Thickener	Solvent Condition	Molecular Diameter (nm)
Hydroxyethyl cellulose I	Water	30.9
	1% SDS	30.9
Hydroxyethyl cellulose II	Water	43.5
Polyacrylamide	Water	23.8
	1% SDS	24.4

between the diameter of HEUR in 0.5% NaCl and HEUR in 1% NaCl, but the difference is significant for HEUR in 0.25% NaCl and HEUR in 0.5% NaCl.

To see if the terminal hydrophobes contribute significantly to the effects of surfactants and electrolyte, the measurements were repeated on a HEUR without terminal hydrophobes. As Table 2 shows, the behavior is the same as for the HEUR molecule itself.

HEUR molecules do contain ''internal'' hydrophobes due to the urethane linkages. To see if these contribute to molecular expansion, previous experiments were repeated with just the pEO backbone. Again, SDS induces a 50% increase in molecular diameter whereas Triton X-405 has little effect on size.

HASE molecules have a low hydrophobe density and very little pEO content, so surfactants should have little effect on their molecular size. Indeed, even a small amount of SDS actually decreases the size of the HASE molecule due to the electrolyte effect. One percent electrolyte has the largest effect on the HASE molecule, reducing the diameter by almost one-half.

As expected, SDS should have little effect on molecular diameter of non-pEO thickeners such as HEC and pAM. This is confirmed in Table 3.

Now that it has been confirmed that anionic surfactants and electrolyte can have a significant effect on molecular size, it is only natural to expect that this would lead to differences in depletion flocculation behavior of latexes. Consequently, the CFC's of a 600 nm model acrylic latex at 0.25 volume fraction were determined using the previously characterized thickeners in a variety of aqueous solutions. As can be seen in Table 4, no flocculation occurs for the associative thickeners in water alone, as expected due to the network structure. Surprisingly, this is also true of the HEUR without terminal hydrophobes and the pEO thickener. This is because the low level of sodium dodecylbenzene sulfonate surfactant used in the latex allows some

Table 4.
CFC's of a 600 nm latex induced by thickeners under various solvent conditions.

Thickener	Solvent conditions	CFC (micromolar)
HEUR	Water	No flocculation
	8% Triton® X-405	134
	1% SDS	46
	1% SDS + 1% NaCl	121
HEUR without hydrophobes	Water	No flocculation
	0.6% Triton® X-405	102
	1% SDS	34
Polyoxyethylene	Water	No flocculation
	0.6% Triton® X-405	27
	1% SDS	13
HASE	Water	No flocculation
	0.1% SDS	1.3
Hydroxyethyl cellulose I	Water	41
Hydroxyethyl cellulose II	Water	14
Polyacrylamide	Water	102
	1% SDS	98

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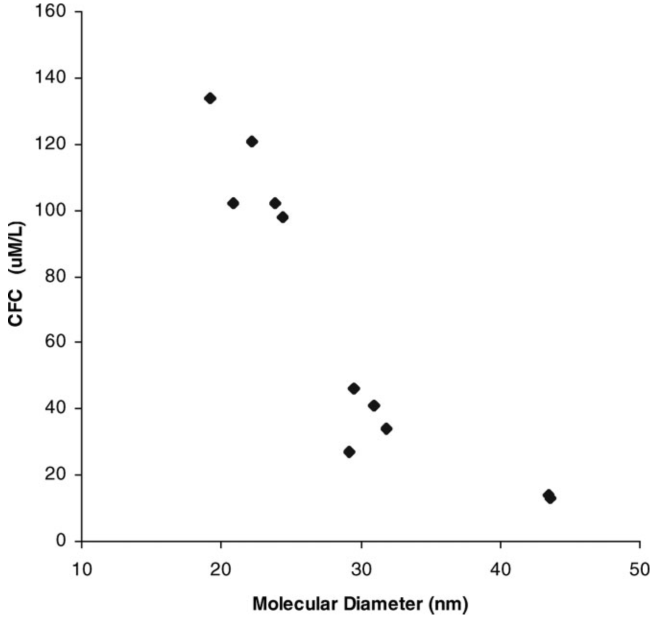

Figure 1.
CFC of a 600 nm latex at 0.25 volume fraction as a function of molecular diameter of the thickener molecules.

adsorption of the pEO chains that is easily destroyed when only a small amount of Triton® X-405 is added. A very large amount of Triton® X-405 is needed in the case of the HEUR thickener. Addition of SDS to the pEO-based thickeners lowers the CFC because of the greatly expanded conformation of the molecules, making them much more efficient flocculation agents. Addition of electrolyte to the SDS-containing systems moves the flocculation behavior back toward systems without anionic surfactant. The flocculation behavior of the non-associative thickeners is little affected by the presence of SDS.

Table 5.
Observed and calculated CFC's for 600 nm latex, grouped by molecular size.

Molecular Diameter (nm)	Mean Observed CFC (μmol/l)	Calculated CFC (μmol/l)
19-24	112	125
29-32	37	30
43-44	13	9

By plotting CFC as a function of thickener molecular diameter, it can be seen that the results separate into three clusters, as shown in Figure 1. As the molecular diameter increases, the CFC decreases, as expected. These results reflect the effect on molecular size rather than molecular composition as a critical factor in depletion flocculation behavior.

Furthermore, when interparticle potential energies were calculated assuming that a -2.7 kT secondary minimum is necessary to induce depletion flocculation,[7] then there was fairly good agreement between the calculated CFC and the observed CFC. These results are listed in Table 5, wherein a zeta potential of -70 m*V* and a particle sheath thickness of 2.3 nm was used for the latex.

Conclusions

Anionic surfactant had a significant effect on molecular size, and consequently latex CFC, for pEO-based polymers. SDS greatly

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expanded the molecular volume of pEO-based thickeners, but not of HEC and pAM. In addition, SDS significantly decreased the molecular volume of HASE thickeners due to the electrolyte effect rather than a surfactant effect. Triton® X-405 nonionic surfactant had little effect on any of the polymers. Electrolyte had a significant effect on the molecular size of polyelectrolyte and pseudo-polyelectrolyte thickeners. NaCl significantly decreased the molecular volume of both pEO-based/SDS systems and HASE systems.

The CFC of a model latex correlated well with polymer and polymer-SDS molecular volume: the larger the molecular volume, the less polymer was needed to induce depletion flocculation of the 600 nm acrylic latex. Calculations of interparticle potential energy including depletion energy correlated well with observed CFC's.

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