Surfactant Behavior and Its Influence On the Viscosity of Associative Thickeners Solutions, Thickened Latex Dispersions, And Waterborne Latex Coatings

David M. Mahli, Mark J. Steffenhagen, Lin-lin Xing, and J. Edward Glass—
North Dakota State University*

Surfactants, varying in their chemical composition and hydrophobic behavior, are used in the formulation of a waterborne coating. These differences influence their aggregation in micellar structures, their interaction with associative thickeners, and in particular, the synergies present in their competitive adsorptions on the disperse phases in a waterborne coating. Adsorption of HEUR thickeners on latexes and the ability of surfactants to displace them from those surfaces is an important variable in the dispersion's viscosity. With large particle latexes, viscosity increases arise primarily from the network built through the interaction of HEURs with surfactants in the aqueous phase. Fluorescence is used to verify the mechanism by which surfactants enhance associative thickener viscosities. That is best achieved with nonionic surfactants, because of their synergies with large hydrophobe HEURs at low concentration. With decreasing latex particle size the adsorbed species is an important contributor to the dispersion's viscosity through its contribution to the latex's effective volume fraction increase and when the size of the adsorbed HEUR is matched to the separation distances of the latex at 0.25 volume fraction. Achieving controlled shear-thinning behavior in small particle size latex paints with the economic constraints on the amount of HEUR required to obtain 90 KU viscosities are discussed.

INTRODUCTION

Surfactants of various types and quantities are present in architectural latex coatings. Long before the introduction of surfactant-modified, water-soluble polymers (associative thickeners), surfactants served various functions that include[1] stabilization of the primary disperse phases (i.e., latex and TiO_2 pigment), wetting of substrates, development of colorant strength, etc. In a coating formulation surfactants do not function alone. There are both competitive and synergistic mechanisms that influence their behavior. An example of the complexity of such interactions includes the influence of coalescing aids on the competitive adsorption of anionic and nonionic surfactants (reported in this journal almost a decade ago.[2]) In the competitive adsorption of sodium dodecyl sulfate (SDS) and a nonylphenol ethoxylate ($NP(EO)_{10}$) in the presence of coalescing aids, the preferential adsorption of the more surface active $NPEO_{10}$ on an acrylic latex is greatest at the onset of micellization and diminishes as the total surfactant concentration increases. The addition of a small amount of coalescing aid decreases the critical micelle concentration (CMC) of SDS but increases the CMC of $NPEO_{10.}$ Background on the type of coalescing aids used in coatings, their solubility in various latex compositions, and their influence on HEUR rheology are found in a prior publication.[3]

Surfactants, in water, aggregate primarily because of the extensive hydrogen bonding of water molecules among their own kind and minimum interaction with the hydrophobes of the surfactant.[4] These aggregates (i.e., micelles) form at a CMC, specific to the structure of the surfactant molecule. It is this behavior that can have a marked effect on the viscosity of coating formulations if they are thickened with associative thickeners. This study will examine the influence of surfactant interactions within the matrix of components in a coating formulation, particularly the latex and thickener, to define

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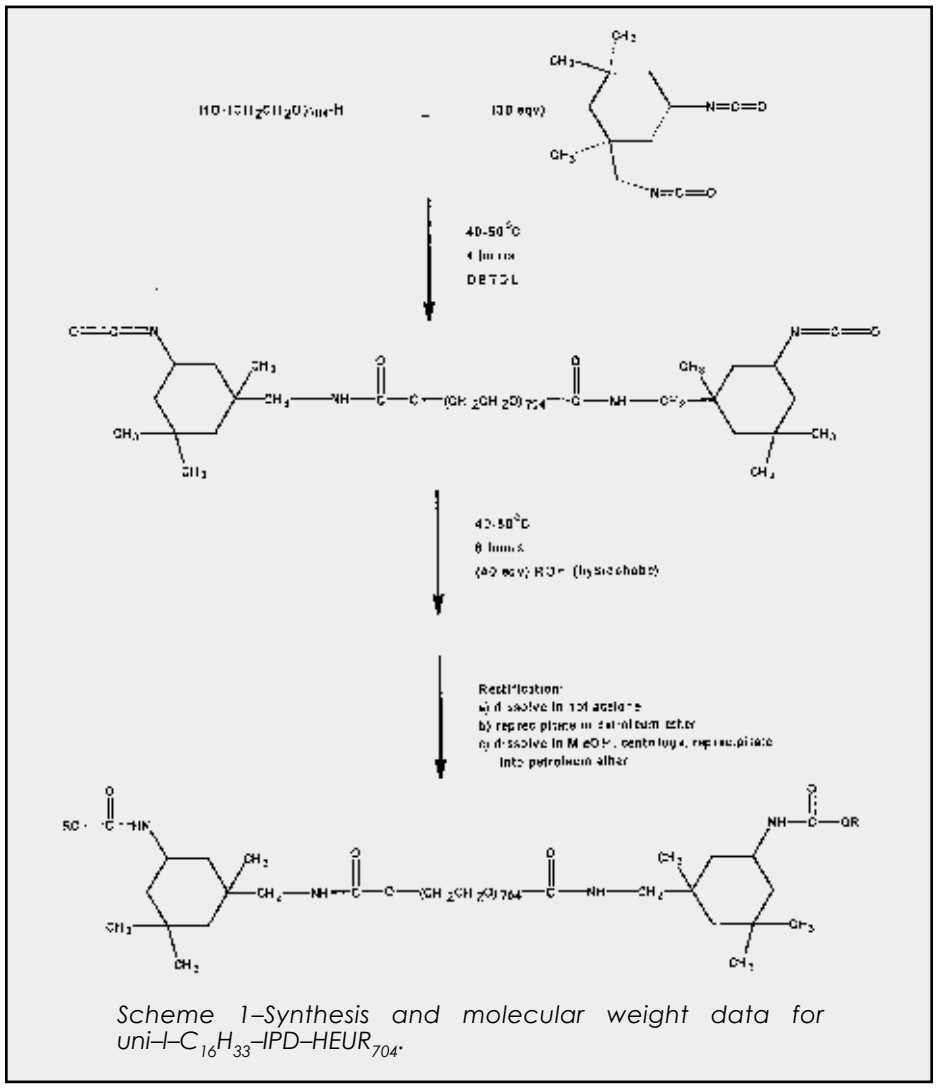
*Polymer and Coatings Dept., Fargo, ND 58103.

their influence on the thickening mechanisms in a waterborne coating. The study will emphasize a model HEUR associative thickener, where the structural aspects are quantitative, to better clarify the mechanisms of thickening.

EXPERIMENTAL SECTION

Synthesis of Hydrophobe Modified Poly(oxyethylene)

Our method of synthesizing model-telechelic HEUR thickeners was defined[5,6] nearly a decade ago and followed since by a number of other investigators. The following thickeners are often described as uni-HEURs to signify that they are not made by a classic step-growth reaction that produces broad molecular weight distributions. The synthesis procedure in this study follows those previously referenced. In the narrow molecular weight distribution synthesis, the reaction sequence uses an excess of diisocyanate to avoid chain extension (*Scheme* 1, stirred for four hours at 45-50°C). The thickeners were purified by dissolution in hot acetone, gravity filtration, precipitation in petroleum ether, and extraction with methanol. This procedure is typically done three times to remove excess diurea and diurethane products due to the excess of diisocyanate.



Scheme 1–Synthesis and molecular weight data for uni–I–$C_{16}H_{33}$–IPD–$HEUR_{704}$.

The procedures involved in the latex synthesis[7,8] and characterization, and in the rheology studies[5,6] have been described. The techniques involved in studying adsorption/desorption phenomena have also been described.[9] In the fluorescence studies, the quencher, benzophenone (+99%), was used as received from Aldrich. The probe, pyrene (+98%, Aldrich), was purified by recrystallization (2x) from absolute ethanol. Solutions for critical aggregate concentration (CAC) measurements were prepared according to the following procedure. The surfactant or thickener solution was weighed into a 20 mL vial and diluted to a 1 g total weight with distilled water. This solution was diluted to 10 g with the filtered pyrene saturated solution, so that the concentration of pyrene was kept constant and less than 10^{-6} M. Solutions for quenching experiments were prepared as follows. A thickener stock solution was prepared by dissolving the powder in pyrene saturated water and rolled in the dark for 24 hr. A portion of these solutions was saturated with benzophenone and the mixtures were put on the roller in the dark for 24 hr. After centrifugation or filtration, aliquots of the benzophenone-saturated solutions were prepared in the concentration range of 0-2*10^{-4} M, and then added to the thickener/pyrene solutions. The UV absorption spectra were recorded with a Hewlett-Packard 8450A diode array spectrometer. Steady-state fluorescence spectra were recorded on a SPEX 2T2 Fluorolog fluorometer using a xenon lamp as the light source and equipped with a DM3000F data system. Fluorescence emission spectra (λ= 350-450 nm) were recorded at room temperature for the probe (pyrene). The excitation wavelength was set at 334 nm and the bandwidths set to 3 nm for excitation and 1.5 nm for emission. The intensity ratios at the first vibronic peak (λ = 372 nm) and at the third vibronic peak (λ = 383 nm) in the pyrene emission spectra, I_1/I_3, were used to determine the CAC of the thickeners. In the determination of a mean aggregation number, N, the ratios of fluorescence intensities in the absence and presence of quencher (benzophenone) were calculated as the ratios of the integrated spectral areas (in wavelength units, from 350 to 450 nm).

With regard to the specific systems used in this study, a dialyzed 108 nm monodisperse acrylic latex stabilized with surface acid groups (accounting for 16% of the

total surface) is studied at 0.25 volume fraction (VF). To the latex, a controlled amount of surfactant (either SDS or $NPEO_{12}$) and 0.5 wt% thickener ($l–C_{16}H_{33}$–IPDI–$HEUR_{704}$) are added. Three well-dispersed pigment grinds are prepared. The pigment grind composition was kept simple and consisted of TiO_2 pigment (Ti-Pure R-900, Al_2O_3 treated), dispersant (either Tamol 731 or Tamol 850), surfactant (either $NP(EO)_{12}$ or SDS), ethylene glycol, and water.[10] Tamol 731 is a diisobutylene and maleic acid copolymer (DIBMA) used at 0.30 g/100 g of TiO_2 and Tamol 850 is polymethacrylic acid (oMAA) used at a 0.39 g/100 g. The concentration of dispersant needed to fully stabilize the pigment particles is determined from dispersant demand curves (viscosity vs. dispersant concentration) and is taken as the minimum point on the curve. The pigment grind formulation used in the current study is given in *Table* 1; for comparison, a standard pigment grind that was used by Lundberg, et al.[10,11] in a typical coating also is given. The objective in this study was to use the minimum amount of dispersant defined by the dispersant demand curve, not the 30X greater concentration to ensure pigment stability normally used by a formulator.

Table 1—Pigment Grind Formulations

Formulation for This Study		Standard Formulation	
Component	**Amount (g)**	**Component**	**Amount (g)**
TiO_2 (R-900)	149.5	TiO_2 (R-900)	149.5
Dispersant: oMMA	1.94g	Dispersant[a]	4.5
Surfactant: $NPEO_{12}$	0.04g (1.20 mM)		
Dispersant: DIBMA	1.79 g	Surfactant[b]	2.0
Surfactant: $NP(EO)_{12}$	0.034 g (1.02 mM)		
or Surfactant: SDS	0.129 g (1.02 mM)		
Ethylene glycol	10.7	Ethylene glycol	10.7
Water	33.0	Water	27.0
Defoamer	0.00	Defoamer	2.6
Total	195.0	Total	196.3

(a) DIBMA
(b) b-$C_{13}H_{27}(OEt)_9$

Table 2—Physical Properties of Surfactants Considered in This Study

	CMC (10^{-3}M)	Aggregation # (N)	Micellar Weight
SDS	8.2	64	18,400
b–$C_{13}H_{26}(OEt)_9$	0.12	164	98,000
NP 12 – Nonylphenol$(EO)_{12}$	0.075	175	131,100
NP 40 – Nonylphenol$(EO)_{40}$	0.10	31	60,900
Brij 700 – $C_{18}H_{37}(EO)_{100}$	0.02	Not Available	NA

The criteria that stability had been achieved in the pigment grinds was a Hegman fineness of grind value >7.0, evaluated after 30, 60, 90, and 120 min of milling. The amount of surfactant in mM concentrations corrects for the volume fraction of pigment. To minimize the amount of surfactant (to a 1:2 ratio of surfactant molecules to dispersant molecules), the current formulation needed slightly more water (33.00 g vs. 27.00 g) to achieve a well dispersed grind. Despite the differences between the current formulation and the standard pigment grind formulation, three well dispersed grinds were obtained using a minimal amount of dispersant and surfactant. These pigment grinds were then used to make fully formulated coatings.

RESULTS AND DISCUSSION

Surfactant/HEUR Synergies on Viscosity Build

Surfactants, even though their behaviors are similar, exhibit differences in micelle properties (*Table* 2). For example, an anionic charge on a surfactant like sodium dodecyl sulfate, SDS, reduces the number of molecules in a micelle (64) when compared with a nonionic surfactant of hydrocarbon equivalence (e.g., 13 carbons and an average ethoxylate length of 9; the micelle contains 164 molecules). This results in different micellular molecular weights (MW), 18,000 and 98,000, respectively. The SDS micelle has an optimum molecular weight for viscosity build in a model HEUR. The MW of the nonionic micelle is the equivalent to a moderate polymer viscosifier, without hydrophobic associations, but neither surfactant viscosifies water in the 1–2 wt% range as an HEUR thickener would do because they do not form networks necessary for viscosity build.

The remaining surfactants in *Table* 2 were included because they have a greater similarity with HEUR thickeners (i.e., larger hydrophobes and/or a larger number of oxyethylene units). In this study, a steady-state fluorescence method with pyrene as the luminescent probe and benzophenone as the quencher has been used. The inflections in the I_1/I_3 emission peaks correspond with the CMC concentrations. This method proposed by Turro and Yekta for anionic micelles[12] has been extended to cationic and nonionic micelles[13] and to polymer-surfactant[14-19] systems. The data in *Figure* 1 are remarkable; the model HEUR is capable of forming hydrophobic domains at concentrations well below the concentrations (CMCs) required for conventional surfactants. The ability to form a hydrophobic domain at these low concentrations, however, does not lead to detectable viscosity increases until there are enough associations to build a large network. In neat aqueous HEUR solutions the viscosity increases do not occur with most commercial thickeners until concentrations >2 wt% are reached. In aqueous solutions, the surfactant can provide nucleation sites to facilitate the participation of at least two hydrophobes from different associative thickeners to build the viscosifying network not observed at the lower HEUR concentrations. This occurs as the surfactant concentration is increased. At a certain concentration a viscosity maximum is reached. With an anionic surfactant this generally occurs between 60 and 80% of the surfactant's CMC. This is a function of the associative thickener concentration. As

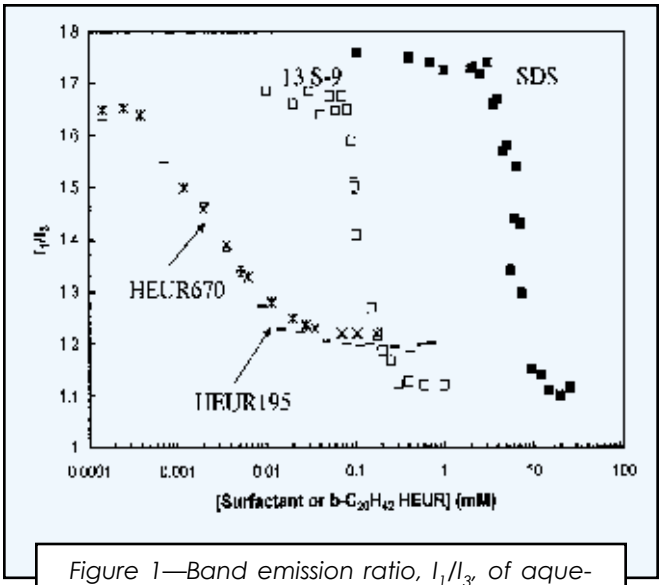


Figure 1—Band emission ratio, I_1/I_3, of aqueous solution of pyrene as a function of b-C_{20} HEURs (of 195 and 670 EO lengths), Tergitol 15 S-9, and SDS concentrations.

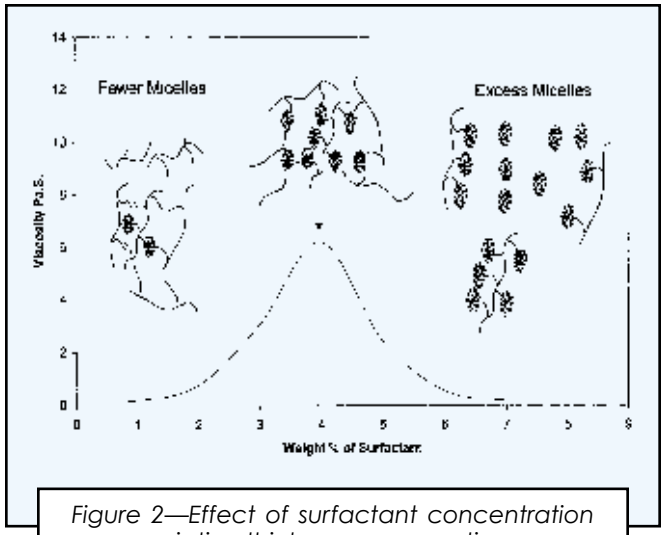


Figure 2—Effect of surfactant concentration on associative thickener aggregation.

the surfactant's concentration is increased beyond that, surfactant micelles surround individual polymer hydrophobes and this disconnects the network (illustrated schematically in *Figure* 2). To the authors' knowledge, this concept was first proposed by Landoll and Sau[20] and embraced by many. There has been no verification of this mechanism. Fluorescence data in support of the surfactant's role in the viscosity build and decrease is provided in *Table* 3. As the concentration of surfactant increases, the number of surfactant molecules in the micelle increases and the number of HEUR hydrophobes in the aggregate decreases, resulting in a decreasing viscosity.

In general, an anionic surfactant like SDS will facilitate a viscosity maximum in solutions of HMHEC or HASE type associative thickeners. In our initial studies[21] of the first model HEUR it was observed that both classical anionic and nonionic surfactants facilitate a viscosity increase of the same magnitude. The conventional nonionic surfactant does not, however, promote significant viscosity increases in HASE or HMHEC aqueous solutions. Nonionic surfactants with very short ethoxylate chains (and limited solubility) effect only small viscosity increases in HMHEC,[22] and with larger hydrophobes and longer $(EO)_{100}$ units in HASE[23,24] thickener solutions.

We have recently observed that the effective terminal size of an HEUR thickener is synergistic with the nonionic surfactant and can result in a dramatic increase in viscosity compared with the increase observed with the anionic SDS surfactant (*Figure* 3). Cationic surfactants will transform from spherical to rod-like micelles as the head size to hydrocarbon ratio increases.[25] The dramatic increase in viscosity as the effective terminal size of the HEUR-hydrophobe increases may be related to such a rod type micelle transition, allowing more HEUR hydrophobes to interlink micelles, but our fluorescence data of HEURs with five different terminal hydrophobe sizes do not support this concept in nonionic surfactants. Anionic SDS mi-

Table 3—Mean Aggregation Number of Mixed Micelles for the Model H_{12}MDI-HEUR at 1.77x10^{-4} M (0.5wt%) with EO_{670} Segment in the Presence of SDS and Tergitol 15 S-9

Thickener's Terminal Hydrophobe	h	SDS (mM)	(micelle)x10^5 (M)	N_s(±1)	N_p(±1)	N_{total} (±1)
I–$C_{12}H_{25}$	Low	0.1	6.0	2	6	8
	Max	2	6.0	33	6	39
	Low	6	11.1	54	3	57
I–$C_{16}H_{33}$	Low	0.1	6.6	2	5	7
	Max	2	7.0	29	5	34
	Low	6	15.4	39	2	41
Thickener's Terminal Hydrophobe	h	**15 S-9 (mM)**	**(micelle)x10^5 (M)**	**N_s(±1)**	**N_p(±1)**	**N_{total} (±1)**
I–$C_{12}H_{25}$	Low	0	6.0	0	6	6
	Max	4	5.9	67	6	73
	Low	10	13.0	77	3	80
I–$C_{16}H_{33}$	Low	0	6.6	0	5	5
	Max	4	6.5	62	5	67
	Low	10	14.1	71	3	74

N_s = # of surfactant in micelle; N_p = # of HEUR hydrophobes in a micelle.

celles are restricted in transforming into rod-like micelles unless the aqueous solutions are saline.[26] Our studies in this area have observed viscosity increases of HEURs in aqueous saline solutions, but the increases are small and may be related to just relative solubility effects.

Whatever the mechanism, the synergy of large viscosity increases in nonionic surfactant solutions containing HEURs with large terminal hydrophobes is real. When multiple hydrophobes are attached to the terminal positions (the synthesis of these latter structural types will be discussed in a later manuscript) this dominance of nonionic surfactants over SDS also is observed.

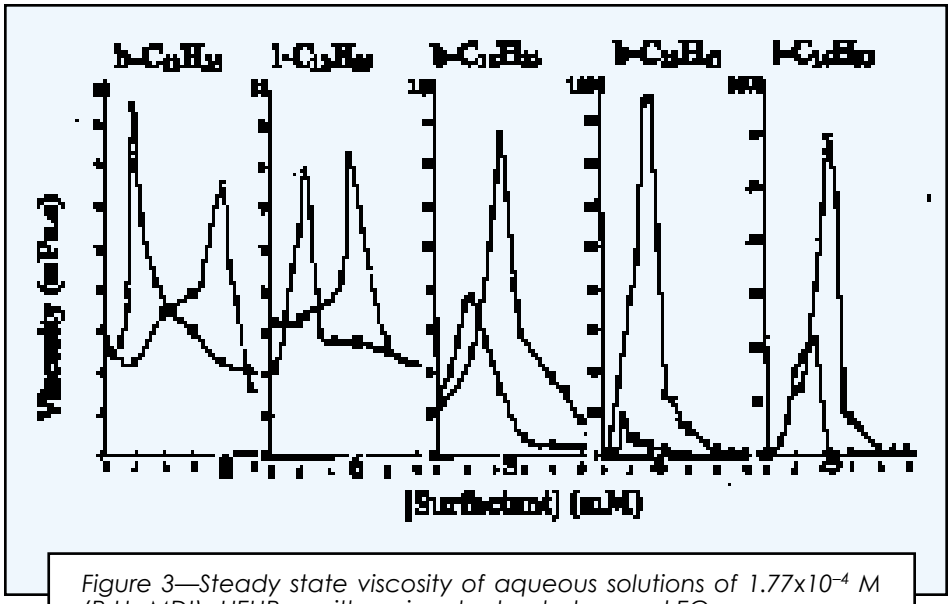


Figure 3—Steady state viscosity of aqueous solutions of 1.77x10^{-4} M (R-H$_{12}$MDI)$_2$-HEUR$_{670}$ with various hydrophobes and EO$_{670}$ spacer as a function of surfactant concentrations. Open symbols SDS and closed symbols Tergitol 13-S-9.

Competitive Interactions at the Latex Interface

Surfactants and HEUR thickeners compete in their adsorption on the disperse phases. This should have a significant influence on the coating's rheological profile. Their interaction with the hiding pigment, TiO_2, is complex and the reader is referred to three prior publications[10,27,28] and a recent one[29] for our contributions in this area. The volume fraction of TiO_2 in a coating formulation is low and although the interactions can influence film gloss, they do not have a significant influence on a coating's viscosity. The latex component is present at a 0.25 to 0.35-volume fraction. In this range, the competitive interactions of associative thickeners and surfactants with latices of different sizes should interplay and markedly influence the dispersion's viscosity. We pursue this course to better understand the role of these interactions on coatings viscosity.

Table 4—Effective Volume Fraction and Relative Viscosity for 108 nm and 600 nm Latices at a Calculated 0.25 Volume Fraction. Influence of Hydration Layers on Effective Volume Fraction

Adsorbed Layer Thickness	Effective Volume Fraction[a]	Relative Viscosity[b]	Viscosity (Pa.s)
600 nm Latex			
5 nm	0.26	2.31	0.006
10 nm	0.28	2.52	0.006
15 nm	0.29	2.64	0.007
20 nm	0.30	2.77	0.007
25 nm	0.31	2.91	0.007
108 nm Latex			
5 nm	0.32	3.05	0.008
10 nm	0.39	4.57	0.011
15 nm	0.46	7.87	0.019
20 nm	0.53	18.15	0.045
25 nm	0.60	120.92	0.302

(a) calculated from equation (1).
(b) calculated from equation (2).

As the volume fraction (VF) of the latex is increased, the viscosity of the disperse phase increases moderately until it approaches a maximum packing fraction, f_m, where the viscosity increases dramatically. In the coatings area the most active promoter of this concept was Mooney.[30] In later studies, Kreiger and Dougherty developed[31] a dimensional analysis approach to quantify the independent influence of various parameters on dispersion rheology. One of the parameters important in understanding the associative thickener/surfactant influence on dispersion rheology is "effective volume fraction"(EVF), a term coined by Kreiger.[31,32] The EVF adjusts the influence of adsorbed surfactant and hydration on dispersion viscosities with increasing VF, defined in the equations below.

$$\phi_{eff} = \phi\left(1 + \frac{6\Delta}{d}\right) \quad (1)$$

where
f_{eff} = effective volume fraction, f = volume fraction, D = adsorbed layer thickness, and d = diameter of latex particle; and

$$\eta_r = \left(1 - \frac{\phi_{eff}}{\phi_m}\right)^{-2.5\phi_m} \quad (2)$$

where h_r is the relative viscosity, and f_m = 0.63 for random packing.

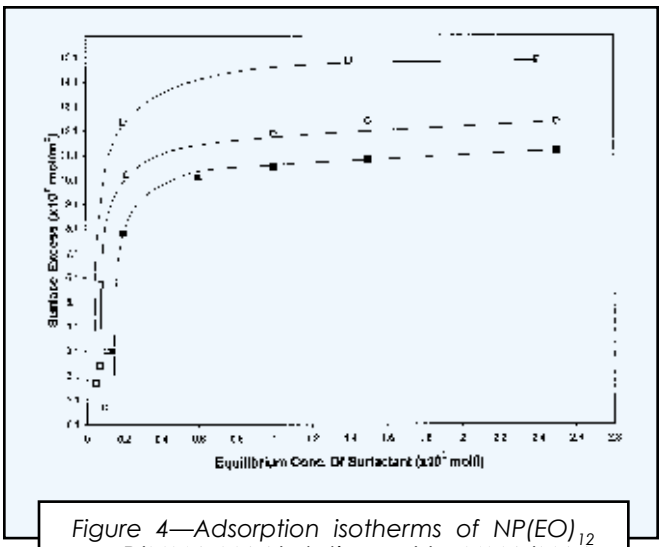


Figure 4—Adsorption isotherms of NP(EO)$_{12}$ on P(MMA-MAA) latices. (¡), MMA/MAA (100/0) latex at pH 6 and 9.5; (¨), MMA/MAA (98/2) latex at pH 6, (n), MMA/MAA (98/2) latex at pH 9.5.

For example, a coating formulated with a 108 nm latex at a volume fraction of 0.25, increases to an EVF of 0.32 with a hydration and/or surfactant/hydration layer of 5 nm (*Table* 4). The methacrylic acid (MAA) segments included in the latex synthesis also expands that hydration layer. If it is assumed the increased expansion is 10 nm, the effective volume fraction increases to 0.39. With a 600 nm size latex the 5 nm increase would increase the EVF from 0.25 to only 0.26; a 10 nm MAA increase would have an EVF of 0.28. There would be only minimal increases in the dispersion's viscosity with the 108 nm latex and no increase in the 600 nm latex (*Table* 4).

At this point we set two arbitrary numbers that relate to reality: the external thickener concentration will be 0.5 wt%. When corrected for the 0.25 VF of the latex the HEUR concentration in the aqueous phase is 0.66 wt%. This is a cost efficiency amount a formulator would expect in a waterborne coating, and is a realistic amount based on our experience in formulating waterborne coatings. We have noted in the synthesis of a 100 nm model latex that a more hydrophobic surfactant in greater amounts is required than in the synthesis of a 220 nm latex.[8] Approximately 0.5 wt% of the synthesis surfactant was present in the aqueous phase after the 100 nm latex synthesis. Analysis of a commercial 100 nm latex revealed that it contained ca. 0.45 wt% residual surfactant in the aqueous phase. This will be restated near the end of this analysis, as an important second criterion.

In this analysis, the limiting surface area that the surfactant occupies is important, as is the adsorption area of the HEUR thickener. These values provide a starting point from which to define parameter boundaries. Additional adjustments are required, for properly stabilized latexes are not planar virgin substrates waiting for adsorbents. The surface of the latex in these studies contains a high density of MAA segments (2 wt% charged in the latex synthesis). In computer simulations based on surface energetics,[33] the incorporation of 5% MAA in the synthesis of styrene copolymer latexes results in a

Table 5—600 nm Acrylic Latex: Distribution of Components in a 0.25 VF Latex with 0.66 wt% Telechelic HEUR in the Original Aqueous Phase

SDS Added to the Aqueous Phase Wt%	mM	SDS Adsorbed (mM)	SDS in Aqueous Phase (mM)	AT Adsorbed (wt%)	AT in Aqueous Phase (wt%)	% AT Desorbed
0	0	0	0	0.49	0.17	0
0.04	1.33	0	1.33	0.49	0.17	0
0.10	3.47	1.10	2.37	0.37	0.29	25
0.20	6.94	2.20	4.74	0.25	0.41	50
0.30	10.40	3.31	7.09	0.13	0.53	75
0.35	12.00	4.41	7.59	0	0.66	100
0.40	13.90	4.41	9.49	0	0.66	100
0.46	16.00	4.41	11.59	0	0.66	100
0.87	30.00	4.41	25.59	0	0.66	100
NP(EO)$_{12}$ Added to the Aqueous Phase Wt%	**mM**	**NP(EO)$_{12}$ Adsorbed (mM)**	**NP(EO)$_{12}$ in Aqueous Phase (mM)**	**AT Adsorbed (wt%)**	**AT in Aqueous Phase (wt%)**	**% AT Desorbed**
0	0	0	0	0.49	0.17	0
0.05	0.66	0.21	0.45	0.44	0.22	9.55
0.10	1.33	0.64	0.69	0.35	0.31	28.65
0.11	1.50	0.69	0.81	0.34	0.32	30.77
0.15	2.00	0.86	1.14	0.30	0.36	38.20
0.18	2.40	0.90	1.50	0.29	0.37	40.0
0.20	2.66	0.94	1.72	0.28	0.38	41.9
0.25	3.33	1.01	2.32	0.27	0.39	44.82
0.30	4.00	1.01	2.99	0.27	0.39	44.82
0.35	4.66	1.01	3.65	0.27	0.39	44.82
0.40	5.33	1.01	4.32	0.27	0.39	44.82
0.80	10.67	1.01	9.66	0.27	0.39	44.82
0.93	12.40	1.01	11.39	0.27	0.39	44.82
1.07	14.23	1.01	13.22	0.27	0.39	44.82
1.24	16.53	1.01	15.52	0.27	0.39	44.82

predominately MAA covered surface. In the current syntheses, the latex compositions are methyl methacrylate (MMA)/acrylate terpolymers containing 2 wt% MAA. The MAA segments are more readily transported to the surface of a MMA latex[34] than they are in a polystyrene copolymer latex particle.

After removal of the latex synthesis surfactant by dialysis, the surfactant [i.e., SDS or $NP(EO)_{12}$] is added back to the latex individually. The incremental amounts added are based on the limiting surface area, A_s, of the individual surfactant, and the surface area of the monodisperse latices. This is a starting point because of the surface MAA segments. An example of the MAA influence on the amount of surfactant adsorbed or desorbed is illustrated in *Figure* 4. Compared to a latex without surface acid groups, the adsorption of nonionic $NP–(EO)_{12}$ surfactant on an MMA latex with MAA segments is greater. This can be attributed to the hydrogen bonding between the ether linkages on the surfactant and the acid groups of the MAA segments.

In the higher pH environment realized in an exterior coating, the neutralized MAA segments will expand and less adsorption occurs (*Figure* 4) relative to a latex without surface segments. The adsorption is significantly less on the same latex when the pH is below 7.0. From these data, the surface area of the MAA surface segments under alkaline pH conditions can be calculated to be ca. 16%. It assumes that the surfactants adsorb individually, not as micelles or more likely as ad-micelles.[35] The two latices (i.e., 108 and 600 nm) examined in this study present different surface areas. At a 0.25 VF, the 108 and 600 nm latexes provide surface areas of $1.16 \cdot 10^{22}$ nm^2 and $2.1 \cdot 10^{21}$ nm^2, respectively, for adsorption. To all of the latex dispersions, 0.5 wt% (0.66 wt% corrected) of the telechelic $(l–C_{16}H_{33}–IPDI)_2$-$HEUR_{704}$ is added. The size of this HEUR is similar to a structure used in previous adsorption studies[9] from which a limiting surface area of 25 nm^2 can be calculated. Adsorption data of a similar molecular weight HEUR capped with octadecyl monoisocyanate units provides[36] an adsorbed layer thickness estimated to range from 8 to 25 nm. Limiting the amount of HEUR in the aqueous phase to 0.66 wt%, there is insufficient thickener to cover the 108 nm particle; however, this amount of HEUR covers the 600 nm latex with a 0.17 wt% excess in the aqueous phase. The limiting surface area (A_s) of SDS and $NP(EO)_{12}$ is 0.79 and 1.55 nm^2/mol, respectively. With adjustments for the surface area occupied by the MAA stabilizers, and the adsorbed HEUR, the amount of each surfactant required to cover the remaining latex surface is given in *Tables* 5 and 6, along with the changes in compositions as the surfactant displaces the HEUR from the latex surface.

Table 6—108 nm Acrylic Latex: Distribution of Components in a 0.25 VF Latex with 0.66 wt% Telechelic HEUR in the Original Aqueous Phase

SDS Added to the Aqueous Phase Wt%	mM	SDS Adsorbed (mM)	SDS in Aqueous Phase (mM)	AT Adsorbed (wt%)	AT in Aqueous Phase (wt%)	% AT Desorbed
0	0	0	0	0.66	0	0
0.06	2.00	2.00	0	0.66	0	0
0.10	3.47	3.47	0	0.66	0	0
0.17	6.00	6.00	0	0.66	0	0
0.20	6.94	6.94	0	0.63	0.03	5
0.30	10.40	10.40	0	0.46	0.20	30
0.35	12.00	12.00	0	0.43	0.23	35
0.40	13.90	13.90	0	0.40	0.26	40
0.50	17.40	17.40	0	0.33	0.33	50
0.55	20.00	18.14	1.86	0.28	0.38	57
0.60	20.80	18.14	2.66	0.23	0.43	66
0.70	24.30	18.14	6.16	0	0.66	100
1.12	40.00	18.14	21.86	0	0.66	100
$NP(EO)_{12}$ Added to the Aqueous Phase Wt%	**mM**	**$NP(EO)_{12}$ Adsorbed (mM)**	**$NP(EO)_{12}$ in Aqueous Phase (mM)**	**AT Adsorbed (wt%)**	**AT in Aqueous Phase (wt%)**	**% AT Desorbed**
0	0	0	0	0.66	0	0
0.28	3.70	3.70	0	0.66	0	0
0.30	4.00	4.00	0	0.66	0	0
0.47	6.25	6.25	0	0.66	0	0
0.55	7.40	7.40	0	0.66	0	0
0.69	9.23	9.23	0	0.66	0	0
0.74	9.89	9.44	0.45	0.59	0.07	10.60
0.79	10.56	9.87	0.69	0.47	0.19	28.79
0.80	10.73	9.92	0.81	0.46	0.20	30.30
0.84	11.23	10.09	1.14	0.41	0.25	37.88
0.87	11.63	10.13	1.50	0.40	0.26	39.39
0.89	11.89	10.17	1.72	0.38	0.28	42.42
0.94	12.56	10.24	2.32	0.36	0.30	45.45
0.99	13.23	10.24	2.99	0.36	0.30	45.45
1.21	16.13	10.24	5.89	0.36	0.30	45.45
1.50	20.00	10.24	9.76	0.36	0.30	45.45
1.63	21.70	10.24	11.46	0.36	0.30	45.45
2.17	29.00	10.24	18.76	0.36	0.30	45.45

FPO

Printer to Place Fig. 5

Figure 5—Low shear rate viscosity for a 0.25 VF, 600 nm acrylic latex with 0.66 wt% telechelic HEUR thickener with varying amounts of surfactant. Gray bars, SDS; black bars, NP(EO)$_{12}$.

Surfactant Influences on the Telechelic HEURs/ 600 nm Latex Viscosities

In the first series of experiments the classical anionic, SDS, and nonionic, NP(EO)$_{12}$, are added individually to the 600 nm latex containing the telechelic HEUR of narrow molecular weight. The MAA segments occupy ~16% of the latex's surface (calculated from the desorption data in *Figure* 4) and it is assumed, for simplicity, that the MAA segments do not interact with the HEUR thickener. In the absence of SDS, the remaining latex surface is partly covered with the 0.66 wt% HEUR originally in the aqueous phase. To interpret the results of adding SDS on the dispersion's rheology, competitive adsorption data of the telechelic-HEUR$_{704}$ on the latex is needed. Data of this type with similar effective hydrophobic terminal groups, but a step-growth product, $C_{10}H_{21}$–H_{12}MDI–HEUR$_{700}$ has been reported.[37] The amounts of SDS incrementally added to displace the amount of HEUR adsorbed are recorded in *Table* 5 (interpolations from *Figure* 7 in reference 37). As the amount of SDS added to the latex/thickener dispersion is increased, the amount of thickener and the amount of SDS in the aqueous phase increases. The amount of SDS promoting viscosity maxima in the aqueous phase is 2-3 mM (*Figure* 3). As SDS is increased above this concentration there is a slow decrease in low shear rate viscosities until the CMC is approached (6 to 8 mM). In this range more thickener is being released to the aqueous phase and the amount of surfactant needed to maintain a viscosity maximum increases. As SDS is increased beyond 7.59 mM, all of the HEUR has been displaced from the latex. With a continual SDS concentration increase a dramatic drop in the dispersion's viscosity at 2s^{-1} is observed (*Figure* 5).

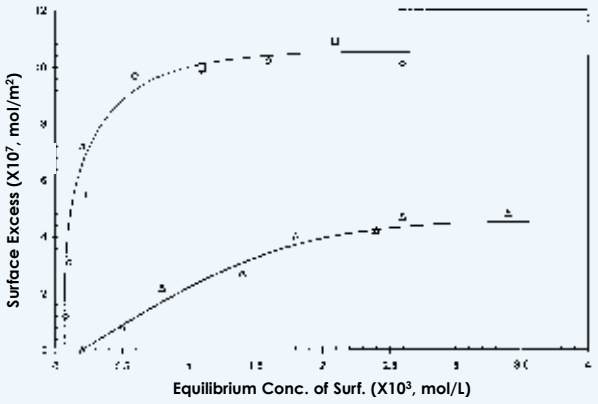


Figure 6—Concentration of NPEO$_{12}$ on the surface of a PMMA/2 wt% MAA latex (⁻), in neat solutions; (··), in 0.4 wt% POE of MW 8000; (D), in 0.4 wt% $C_{16}H_{33}$-IPDI-HEUR$_{704}$.

The scenario of incremental increases in surfactant concentration was repeated with the nonionic surfactant, NP(EO)$_{12}$, which has a limiting surface area of 1.55 nm^2/mol. The adsorption data for the NP(EO)$_{12}$/telechelic HEUR were obtained from our studies in *Figure* 6. In these studies, the amounts of NP(EO)$_{12}$ desorbed from a surfactant saturated surface, due to HEUR adsorption, is measured by UV analysis. Interestingly, POE does not adsorb on the surface of the latex saturated with surfactant (*Figure* 6). Despite a lower CMC than SDS (*Table* 2) the viscosity maxima in the aqueous solution has always occurred at a higher mM surfactant concentration with this nonionic surfactant (*Figure* 3). Tabulations of the thickener and surfactant distributions are recorded in *Table* 5, and the low shear rate (2s^{-1}) viscosity data for component variations are listed in *Figure* 5. The NP(EO)$_{12}$ data in *Table* 5 is a little different than the influence of SDS on HEUR desorption reported in reference 37. The nonionic surfactant does not result in total displacement of the HEUR thickener, within the concentration limits used in waterborne, latex coatings. Comparisons between surfactants reveal why the HEUR viscosities with the nonionic are higher. With the addition of 3.47 mM SDS, there is 2.37 mM in the aqueous phase. This is at the viscosity maximum concentration for the small amount (0.29 wt%) of HEUR in the aqueous phase. The addition of 2.0 mM NP(EO)$_{12}$ (*Figure* 5) places 1.14 mM in the aqueous solution where a plateau maxima in the amount of HEUR (0.36 wt%) in the aqueous phase begins. The 1.14 mM of the nonionic surfactant in the aqueous phase is near the viscosity maximum concentration (2.75 mM, *Figure* 3) and it is in this region that the highest viscosities (*Figure* 5) are observed. With more surfactant there is a small amount of HEUR desorbed into the aqueous phase, but the increasing surfactant concentration begins to disrupt the HEUR association network. The viscosities of the SDS solutions are lower than the nonionic surfactant because there is less HEUR in the aqueous solution with SDS at its viscosity maximum concentration and the nonionic surfactant has a greater synergy in facilitating a higher viscosity maximum (*Figure* 3).

Surfactant Influences on the Telechelic HEURs/108 nm Latex Viscosities

The distributions of components in the 108 nm latex study are given in *Table* 6; the low shear rate (2s^{-1}) viscosities are illustrated in *Figure* 7. The smaller particle

has a much larger surface area that can accommodate almost everything put in the dispersion. As previously observed, the MAA segments account for ~16% of the surface. For simplicity, it can be assumed that all of the HEUR, based on its size, can be adsorbed on the surface, with room (59%) for surfactant adsorption (assuming that the thickener would not spread out on a sparsely populated surface). HEUR displacement from the latex surface would not occur until 7 mM of SDS has been added.[37] Under this simplistic approach, the aqueous solution would not contain significant amounts of SDS to promote viscosity build until more than 20 mM of SDS has been added to the dispersion. To displace the HEUR from the latex surface, 24 mM of SDS is required. In contrast to the 7 mM of SDS, 9.2 mM of the nonionic surfactant is required for surface coverage of the latex (*Table* 6), and greater amounts of $NP(EO)_{12}$ in the aqueous phase are required to assist in the network formation of the desorbed HEUR. The concentration of surfactant in the aqueous phase will be higher than calculated because of equilibrium distribution of the components between phases. There will always be greater amounts of HEUR in the aqueous phase in SDS solutions. Within the range of concentrations used in waterborne coatings, the nonionic will not displace all of the adsorbed HEUR. The low shear rate ($2s^{-1}$) viscosities with the 108 nm latex are higher than those with the 600 nm latex (*Figures* 5 and 7), irrespective of the surfactant used. The solution network contributions to viscosity build cannot explain this difference. For example, at comparative 10.5 mM surfactant additions there is 0.55 and 0.39 HEUR in the aqueous phase; however, with the small 108 nm latex at these respective SDS and $NP(EO)_{12}$ levels the amounts of HEUR in the aqueous phase is 0.20. The lower HEUR concentrations in the aqueous phase are not consistent with the higher viscosities of the smaller latex.

The EVF concept as proposed in *Table* 4 does not provide full support for the viscosity differences noted between the two latex particle sizes. For this we modify the EVF concept with interparticle distances. Interparticle interactions are magnified at high volume fractions and the particle size of the latex can play an important role in defining the viscosity response. The relationship between the interparticle distance, d_{sep}, the particle diameter, d, and volume fraction, f, is given in equation (3).

$$d_{sep} = d\left[\left(\frac{\phi_m}{\phi}\right)^{\frac{1}{3}} - 1\right] \qquad (3)$$

Calculations for the average separation between two particles for various adsorbed layer thicknesses for a 600 nm and a 108 nm latex are given in *Table* 7. A packing fraction, f_m, of 0.63 is used in the calculations. There are electrostatic forces that can possibly influence the viscosity difference but the adsorption of an HEUR will minimize such effects as illustrated in *Figure* 8.

From the EVF concept, the adsorption of the HEUR thickener onto the latex's surface, in the closer proximity of the 108 nm particles, alters the viscosity, but on a marginal scale (*Table* 4); however, the smaller particle separation distances with the size of the adsorbed HEUR in the range of the particle separation distances can promote interbridging of particles. This is reflected in a more viscous solution with a higher elastic component[38] (i.e., G', the storage modulus, *Figure* 9). With the 600 nm latex, the interparticle distances are between 158 to 203. Previous dynamic light scattering studies in our group[39] have shown that at 0.36 wt% of an HEUR, equivalent to that studied in this contribution, contain HEUR aggregates that are roughly 200 nm in size. This suggests that some interparticle bridging may occur, albeit to a much lower extent than with the 108 nm latex, with the 600 nm latex, explaining its relative low storage modulus response. Without the HEUR thickener, both the 600 and 108 nm latices exhibit Newtonian flow.

In our previous studies of large hydrophobe HEURs

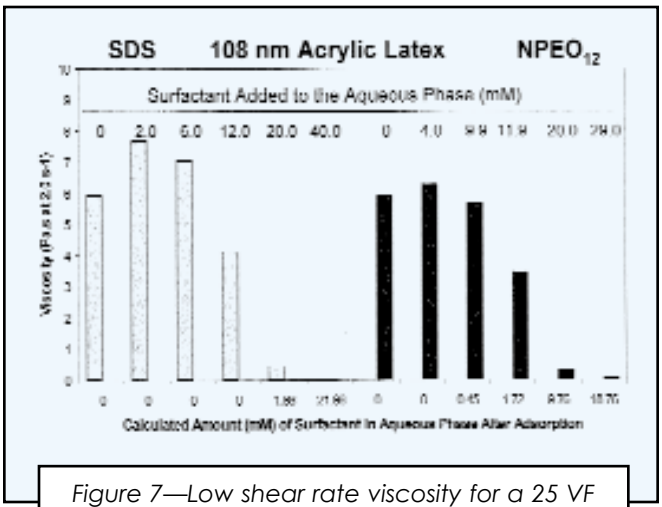


Figure 7—Low shear rate viscosity for a 25 VF 108 nm acrylic latex containing 0.66 wt% telechelic HEUR thickener with varying amounts of surfactant. Gray bars, SDS; black bars, $NP(EO)_{12}$.

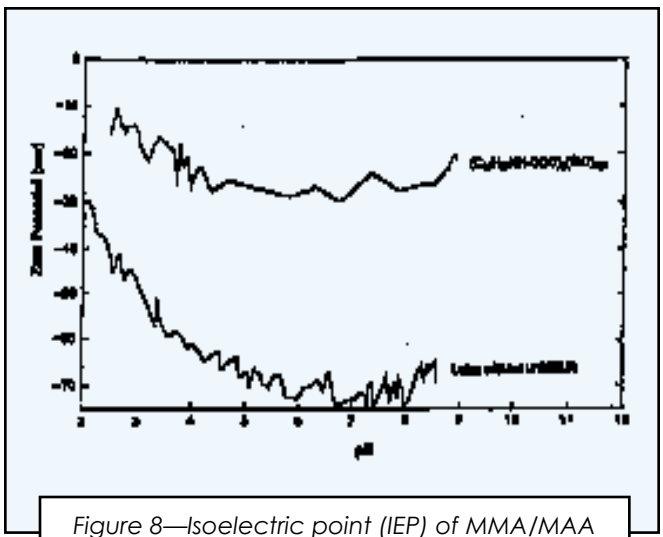


Figure 8—Isoelectric point (IEP) of MMA/MAA (96/4) latex with 0.05 wt% model associative thickener $(C_{18}H_{37}NH\text{-}COO)_2(EtO)_{454}$ at pH = 9.2.

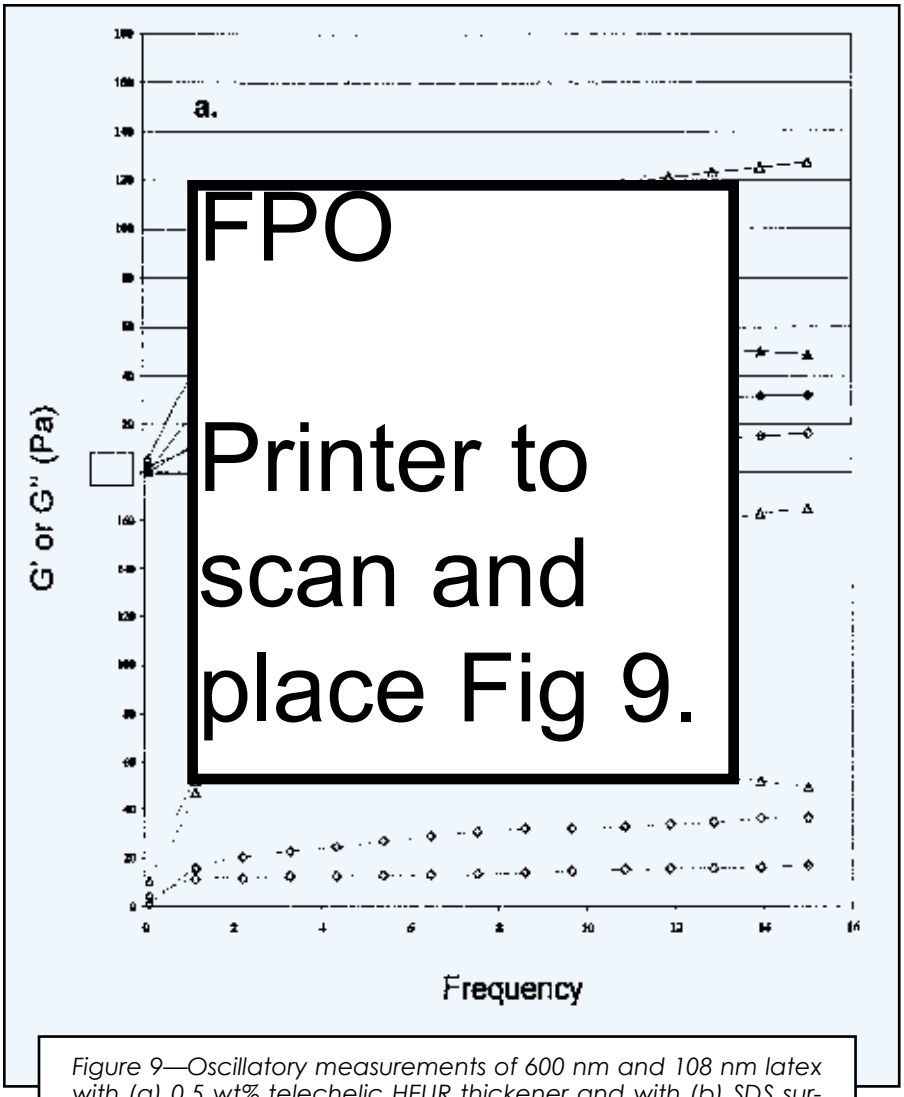


Figure 9—Oscillatory measurements of 600 nm and 108 nm latex with (a) 0.5 wt% telechelic HEUR thickener and with (b) SDS surfactant. Open symbols = G'; Closed symbols = G''. (a) ⁻, 600 nm, no surfactant; D 108 nm, no surfactant; (b) ⁻, 600 nm, 1.33 mM SDS; D 108 nm, 2 mM SDS.

coupled with H_{12}MDI, a more hydrophobic diisocyanate than the IPDI used in this study, gel-like aqueous solutions were observed. They gave discontinuous flow curves similar to those observed in *Figure* 10 which contain latex. The viscosity shear rate profiles in *Figure* 10 combined with the data in *Tables* 5-7 support an interparticle bridging mechanism at low surfactant levels. The HEUR thickener adsorbed on the dialyzed 108 nm latex has not been displaced by the 7 mM of SDS added. The interaction of adsorbed HEURs with other latex particles provides a very shear thinning dispersions, with an inflection riddled shear rate profile due to the interparticle interactions. The addition of 19 mM SDS to the 108 nm latex produces a smooth transition. Slightly over 50% of the HEUR has been desorbed and SDS is beginning to appear in the aqueous phase. The flow exhibits a Newtonian behavior at low shear rates with the shear thinning beginning around 10 s^{-1}. There is over 1 mM of SDS in the aqueous phase to network 57% of the HEUR that has been desorbed. Such networks have a relaxation time of 0.1 sec, allowing the low shear rate Newtonian plateau. The relatively low decrease in viscosity with shear rate is also related to the disruption of latex aggregates with a decreased amount of interbridging.

With the 600 nm latex, an incremental amount of SDS (3.47 mM) addition displaces 25% of the adsorbed HEUR and 2.36 mM of SDS is in the aqueous phase, to promote aggregate formation. The flow profile is similar to the 108 nm latex with a larger amount of SDS. As the DLS data[39] mentioned previously notes, there are 50 and 200 nm sized aggregates in aqueous HEUR solutions. The larger aggregates could interbridge the 600 nm latex, but there would be fewer, less effective bridges than observed in the 108 nm latex at low surfactant concentrations.

When a large amount of SDS (16 mM) is added to the 600 nm latex, all of the HEUR has been desorbed but the concentration of SDS is beyond that promoting a viscosity maximum in the aqueous phase. Without contributions from a network in the aqueous phase or from latex interactions, the viscosity is low. The low shear thinning behavior is likely associated with the behavior of electrostatic forces. The latex has negative charges associated with adsorbed SDS and the ionized MAA surface segments, neither shielded by adsorbed HEUR, and the HEUR thickener in the aqueous phase has become a polyelectrolyte by interacting with the excess SDS. It is unlikely to be related to depletion flocculation effects because of the low molecular weight of unassociated HEURs.

Fully Formulated Coatings

To bring this study to completion, pigmented (TiO_2) latex coatings were prepared. Normally the pigment grind brings an excess of surfactant into the coatings formulation. A minimum dispersant/nonionic surfactant concentration, described in the experimental section, was used. The paint formulations (an adaptation from Lundberg[11]) were kept as simple as possible (.07 VF pigment and 0.25 VF latex thickened to ~90 Kreb unit (KU) "viscosity"). The amounts of $(l–C_{16}H_{33}–IPDI)_2$-$HEUR_{704}$ and $NP(EO)_{12}$ surfactant that adsorb onto the DIBMA stabilized pigment were determined from previous adsorption data.[10,28,29] A total of eight fully formulated coatings were made using the 108 nm dialyzed latex, the pigment grinds, and varying concentrations of SDS or $NPEO_{12}$. Even though the concentrations and number of components put into these formulations has

been kept to a minimum, these are not simplistic systems due to the numerous interactions between the various components. There are pigment/dispersant, dispersant/surfactant, thickener/dispersant, thickener/latex, and surfactant/latex interactions, all occurring simultaneously.

The data in *Figure* 11 are presented from a formulator's viewpoint: how do the controlled surfactant variations influence the amount of thickener required to achieve a 90 KU viscosity in a small 108 nm latex formulation? The goal is to add 0.5 wt% to achieve the 90 KU. In the coating, 0.07 VF of TiO_2 is added. It is assumed that the optimum surfactant/dispersant concentration described in the experimental section has not added any extra of these components to the aqueous phase of the coating. If the oligomeric methacrylic acid (oMAA) is used to stabilize TiO_2, the interaction of the thickener with the hydrophobes of the DIBMA stabilizer is lost and more HEUR is required with this stabilizer (*Figure* 11) to reach 90 KU. However, the amounts of HEUR needed to achieve 90 KU are low when low mM concentrations of $NP(EO)_{12}$ are used with either pigment stabilizer for TiO_2.

The viscosity dependence on shear rate of the formulations containing $NP(EO)_{12}$ with the DIBMA/TiO_2 pigment grind are illustrated in *Figure* 12. The viscosity/shear rate profiles decrease in their shear thinning behavior with increasing surfactant concentrations. Increasing amounts of HEUR are required with increasing surfactant to maintain a 90 KU. At 15.7 mM of $NP(EO)_{12}$, 45% of the HEUR has been displaced, but the 6.54 mM of nonionic surfactant in the aqueous phase is at the optimum concentration to facilitate a viscosity maximum with the 0.11 wt% HEUR in the aqueous phase. When 15.72 mM of $NP(EO)_{12}$ is added to the formulation (using the DIBMA dispersant) the arguments used before seem applicable with the $NP(EO)_{12}$ surfactant; however, in the addition of this amount of SDS, a large increase in HEUR concentration (0.85 wt%) is required to achieve 90 KU. Considering that this formulation contains TiO_2, this is a little surprising when compared to the appropriate data in *Figure* 10. The 0.85 wt%, not corrected for the latex and pigment phase volume fractions, is well beyond that related to the model data extrapolation in *Table* 6, so the distribution of the surfactant and HEUR is uncertain.

Returning to the nonionic surfactant, $NP(EO)_{12}$, more than twice this level of nonionic surfactant (i.e., 36.3 mM) results in ~20 mM in the aqueous phase which is ~ to 0.5 wt%, the second criterion noted earlier as the amount in the aqueous phase after synthesis of a 100 nm latex. The rheology profile again decreases in shear thinning, with the amount of HEUR at the 0.5 wt% level. The transition of $NP(EO)_{12}$ from spherical to rod-like structures[40] and its interaction with the large hydrophobe HEUR is probably contributing to this rheology profile.

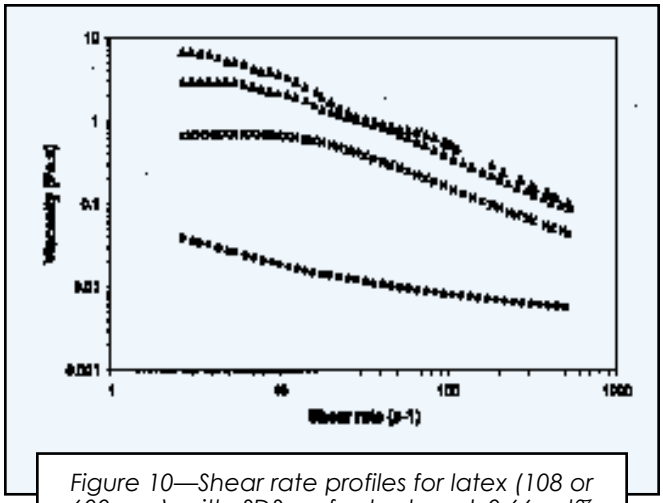


Figure 10—Shear rate profiles for latex (108 or 600 nm) with SDS surfactant and 0.66 wt% HEURs (telechelic or comb). (D), 108nm latex, 7 mM SDS and I–$C_{16}H_{33}$–IPDI-telechelic $HEUR_{704}$, (p), 600nm latex, 3.47 mM SDS and I–$C_{16}H_{33}$–IPDI– telechelic $HEUR_{704}$, (x), 108nm latex, 19mM SDS and I–$C_{16}H_{33}$–IPDI– telechelic $HEUR_{704}$, (u), 600nm latex, 16mM SDS and I–$C_{16}H_{33}$–IPDI– telechelic $HEUR_{704}$.

Finally, we include a coating made with many of the same components, but formulated to a more realistic[41] 0.39 VF, 0.32 VF of a small latex and 0.07 VF TiO_2. This is closer to an actual waterborne, latex coating. There is 0.7 wt% surfactant on the latex; 0.5 wt% (6.7 mM) in the aqueous phase and it is thickened with a step-growth $C_{10}H_{21}$–H_{12}MDI–$HEUR_{700}$HEUR. The efficiency (i.e., 0.49 wt% to obtain 90 KU) is remarkable considering that the thickener is a step-growth HEUR.[6] In this formulation, there is an excess of surfactant and a 30% excess of the hydrophobic alpha-olefin/maleic acid stabilizer that may interact with the HEUR thickener and surfactant, in rod-like aggregates, to provide viscosity. As noted in the introduction, coalescing aids can influence the preferential adsorption[2] of surfactants and one is included at the usual 7% level. There are many factors that can influence the viscosity of the coatings. This area demands significantly more experimental work.

Table 7—Calculations for the Average Separation Between Two Particles for Various Adsorbed Layer Thicknesses for 600 nm and 108 nm Latices

Latex Particle Size	Adsorbed Layer Thickness	Effective Volume Fraction	Average Separation Between Two Particles
600 nm			
	5	0.263	203
	10	0.275	191
	15	0.288	179
	20	0.300	168
	25	0.313	158
108 nm			
	5	0.319	26
	10	0.389	18
	15	0.458	12
	20	0.528	6.3
	25	0.597	1.9

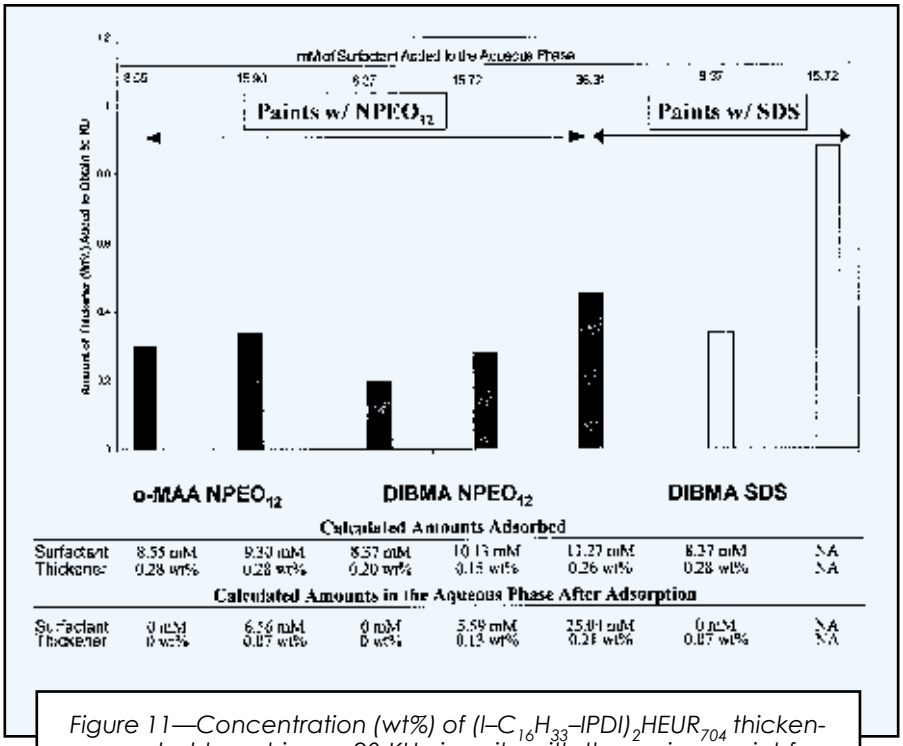


Figure 11—Concentration (wt%) of (I–$C_{16}H_{33}$–IPDI)$_2$HEUR$_{704}$ thickener needed to achieve ~90 KU viscosity with the various paint formulations (coating contains the 108 nm dialyzed latex (0.25 VF) and stabilized TiO_2 pigment (0.07 VF).

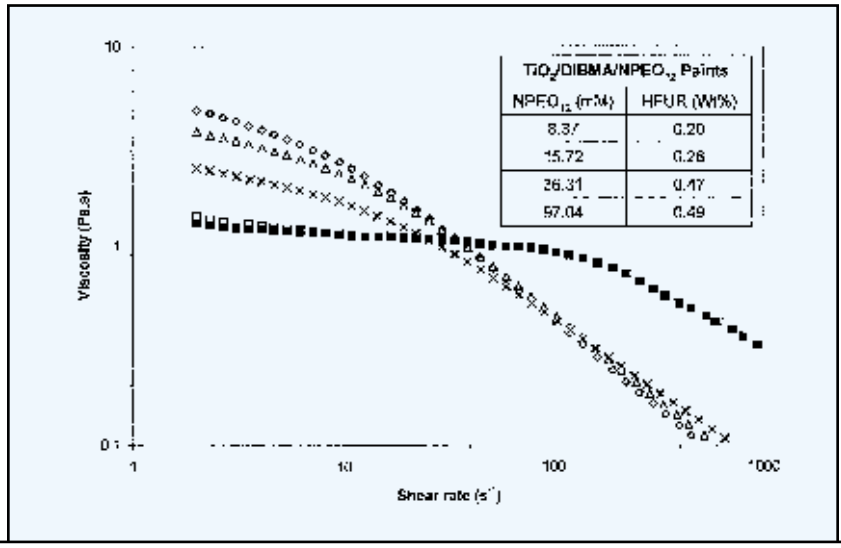


Figure 12—Viscosity dependence on shear rate for TiO_2/DIBMA/NP(EO)$_{12}$ coatings with various concentrations of NPEO$_{12}$ and (I–$C_{16}H_{33}$–IPDI)$_2$-HEUR$_{704}$ thickener.

	mM Surfactant Added	*[a]mM NPEO$_{12}$ aqueous phase*	*Total wt% AT*	*wt% AT adsorbed*	*[a]wt% AT aqueous phase*
(⁻)	*8.37*	*0*	*0.20*	*0.20*	*0*
(D)	*15.72*	*5.59*	*0.28*	*0.15*	*0.13*
(x)	*36.31*	*25.04*	*0.47*	*0.26*	*0.21*
[b](¨)	*97.04*	*85.86*	*0.49*	*0.27*	*0.22*

Open symbols, 3 min. ramp up; closed symbols, 3 min. ramp down.
(a) Calculated values after adsorption; (b) Typical coating formulation with a step-growth (I–$C_{10}H_{23}$–H_{12}MDI–STEP–GROWTH–HEUR$_{700}$) thickener and b–$C_{13}H_{27}$–(EtO)$_9$ nonionic surfactant that we have used in previous studies.

CONCLUSIONS

Fluorescence is used in this study to verify the mechanism by which surfactants enhance associative thickener viscosities. Additional observations on the uniqueness of nonionic surfactant enhancement of HEUR solution viscosities at low HEUR concentrations are reported. Adsorption of HEUR thickeners on latexes and the ability of surfactants to displace them from those surfaces is dependent on the total surface area of the latex at a given volume solids. Displacement of HEURs from 600 nm latexes provides HEURs in the aqueous phase, that networked by surfactant provide the primary source of viscosity. This is best achieved with nonionic surfactants, because of their synergies with large hydrophobe HEURs at low concentration. With 108 nm latexes, the adsorbed species is an important contributor to the dispersion's viscosity through its contribution to the latex's effective volume fraction increase and when the size of the adsorbed HEUR is matched to the separation distances, d_{sep}, of the latex at 0.25 volume fraction. Complete displacement of adsorbed HEURs by a typical formulation nonionic surfactant does not occur and is therefore less sensitive to formulation mischarges in small latex, waterborne coatings. This study was conducted with a telechelic HEUR. Similar results were observed with a comb-HEUR architecture but were not discussed due to the length of this article.

There are several assumptions made in this article that we know are not true. For example, an HEUR thickener interacts with the MAA acid stabilizing units. The associative thickener does interact with the pigment when it is stabilized with a dispersant. All of the components will exist in equilibrium to some extent in and on all phases. Nevertheless, there is a general correlation in this analysis between median particle size of the latex, classical anionic and nonionic surfactants, and the hydrophobe structure of HEUR thickeners on the rheological response of component combinations used in a waterborne coating when the competitive adsorption of the components is considered. This is not an all-encompassing analysis, but it is the first.

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