Functional Polymers for Colloidal Application. VIII. Syntheses of Anionic and Zwitterionic Aniline–Formaldehyde Condensates and Their Dispersing Ability to Zwitterionic Clay

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SYNOPSIS

Anionic and zwitterionic aniline–formaldehyde condensates have been synthesized by a methylenation under mild reaction conditions and a reaction with propane sultone. The formation of condensates is characterized by NMR, i.e., the peak of methylene at δ = 3.5–4.0 ppm and the peaks of propylsulfonate at δ = 2.7–3.4 ppm and δ = 1.7–2.2 ppm. The results from GPC show that a longer condensation time increases the degree of polymerization of the condensates. The dispersing properties of the condensates are assessed by the viscosity, scanning electron microscopy (SEM), and adsorption behaviors. N,N-dimethyl-N-(3-propylsulfonate)anilinium–formaldehyde condensates (DPSAF) with higher molecular weight (DPSAF-H) show significantly lower apparent viscosities. Comparing the results of SEM and the viscosity method, it can be concluded that, under comparable conditions, a suspension with a lower viscosity is more homogeneously dispersed. The amount of DPSAF-H adsorbed onto clay is significantly higher than that of PSAF-H at low concentrations of the dispersant and reaches an optimum after ca. 3 wt %. This result is in parallel with the trend of viscosity. The zwittionic DPSAF promotes their dispersing ability of clay in water due to the existence of the positive and negative charges. The decrease in the amount of adsorbed PSAF-H with increasing pH can be interpreted by the increased negative charge of the clay, as a result of the decreased interaction between the anionic PSAF-H and the clay. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Dispersing technology has been widely studied both for academic and industrial purposes. It is diversely applied both in conventional industries[1-3] (such as coatings, pigments, and agriculture) and high-tech industries[4] (such as magnetic slurry and photo applications). When particles are dispersed in solution, the system is thermodynamically unstable; thus, dispersants are normally used to stabilize the system. The main function of the dispersant is to provide the particles with an electrostatic barrier[5] and/or with steric hindrance[6] to prevent the coagulation of the particles.

In addition to surfactants and polymers, naphthalenesulfonate formaldehyde condensates (NSF) are used as industrial dispersants. Because of the strong interaction of NSF with polar and nonpolar surfaces, NSF have been widely used for dispersing dyes, coal, and cement in aqueous systems.[7-9a-c,10,11] For dispersing polar particles such as cement, the adsorption of NSF on polar surfaces arises mainly from the interaction between the polarizable naphthalene ring and the polar surface.[12] Aniline also has an aromatic ring and polar amino group; therefore, it can be expected to interact with the polar particles. Particularly for clay, the plates of the particles carry negative charges on the basal surfaces and with positive (low pH) or negative (high pH) charges at the edge in aqueous suspension.[13] If the amino group of the aniline is converted into an ionic group, its condensates can interact with clay more efficiently and can be used as a dispersant.

In this study, anilines are reacted with formaldehyde to form condensates first, and then the amino group is reacted with propane sultone to carry an anionic or a zwitterionic hydrophilic group (as shown in Scheme 1). The anionic and zwitterionic aniline–formaldehyde condensates are used as dispersants to disperse clay in aqueous solutions. The dispersing ability is assessed by viscosity methods and scanning electron microscopy (SEM) and correlated with the adsorption phenomena. These results are used to illustrate the relations between the charge properties of the condensates and their dispersing ability.

EXPERIMENTAL

Materials

Aniline (Wako, EP grade), N,N-dimethylaniline (Wako, EP grade), formaldehyde solution (Merck, 37 wt %, EP grade), and propane sultone (Tokyo Kasei, GR grade) were used without further purification. C.I. Navy Blue 79 (E-Hwa Co., with a BET surface area of 4.85 ± 0.03 m^2/g), C.I. Brown 1 (E-Hwa Co., with a BET surface area of 1.53 ± 0.04 m^2/g), and clay (Akima 35, a kaolinite, with a content of SiO_2 of 48.57%, and of Al_2O_3, 36.92%) were used as supplied. The water used in these experiments is ion-exchanged and distilled, with pH between 6.8 and 7.2 and a conductivity of 4.4 $\times 10^{-6}$ Ω^{-1} m^{-1}.

Methods

Synthesis and Characterization of Condensates

(a) **Synthesis of N-(3-sodium propylsulfonate)aniline–Formaldehyde Condensates (PSAF) (Scheme 1).** In a 500 mL reaction kettle, formaldehyde (37%, 48.7 g) was added to a mixture of aniline (93 g) and HCl (28%, 39.4 g) over 50 min. Condensation was carried at 95–100°C for 1 and 2 h. The temperature was decreased to 60°C and the mixture was neutralized with NaOH (38.8%, 32.2 g) and washed in warm water three times, followed by separation of the oil phase from the aqueous layer. The unreacted aniline was separated and water was removed at 170°C under the reduced pressure of 15 mmHg. Then, the residue was dissolved in a mixed solvent of 90% phenol and 10% acetone (150 g). To this solution, propane sultone (130 g) was added dropwise, and the temperature was increased to 70–
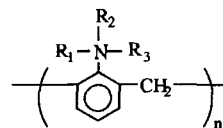
(1)
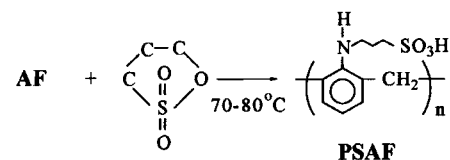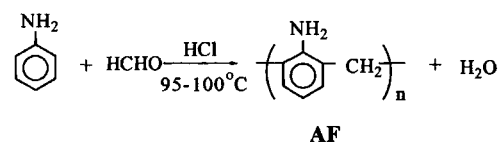
(2)
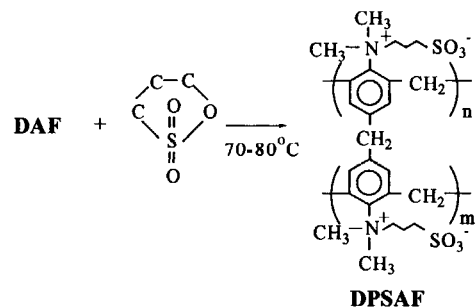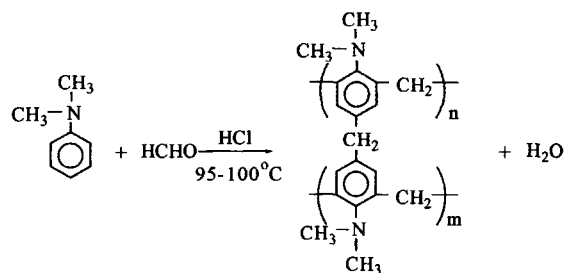
(3)

PSAF : R_1 = none, R_2 = H, R_3 = —(CH$_2$)$_3$SO$_3$Na

DPSAF : R_1, R_2 = —CH$_3$, R_3 = —(CH$_2$)$_3$SO$_3^-$

Scheme 1 Syntheses of N-(3-sodium propyl sulfonate)aniline–formaldehyde condensate (PSAF) and N,N-dimethyl-N-(3-propyl sulfonate)anilinium–formaldehyde condensate (DPSAF).

Table I   Reaction Conditions for Synthesizing the Dispersants[a]

Dispersants	HCHO/Monomer/HCl (Molar Ratio)	Relaxation Time (h)	
		Condensation[b]	Opening[c]
PSAF-L	0.4/1.0/0.3	1.0	5.0
PSAF-H	0.6/1.0/0.3	2.0	5.0
DPSAF-L	3.0/1.0/1.0	5.0	8.0
DPSAF-H	3.0/1.0/1.0	10.0	8.0

[a] The data cited are from Ref. 13.
[b] The reaction temperature for condensation was maintained at 95–100°C.
[c] The reaction temperature for the ring-opening of propane sultone was maintained at 70–80°C.

80°C to react for 5 h. After reaction, the mixture was poured into acetone. The precipitate was dissolved in water and the pH of the solution was adjusted to 9–10. The water was evaporated and the residue was reprecipitated in acetone again to obtain the 154 g of product (Table I).

(b) Synthesis of N,N-Dimethyl-N-(3-propylsulfonate)anilinium–Formaldehyde Condensates (DPSAF) (Scheme 1). N,N-Dimethylaniline (61.0 g) and HCl (30% 51.0 g) were mixed, and formaldehyde (37%, 121.6 g) was added to the mixture over 50 min. The mixture was heated to 95–100°C and refluxed for 8 h. Then, the temperature was decreased to about 60–70°C, and an aqueous solution of NaOH was added to neutralize the HCl. The mixture was washed in water, and the water phase was poured out and dried in a vacuum oven for 5 h. Then, the residue was dissolved a mixed solvent of 90% phenol and 10% acetone (150 g). To this solution, propane sultone (61.0 g) was added dropwise, and the mixture was heated to 70–80°C to react for 5 h. After the reaction, the mixture was evaporated, then poured into acetone for reprecipitation to obtain 95.0 g of product (Table I).

(c) Characterization of Condensates. PSAF and DPSAF dissolved in D_2O were characterized by ^{1}H-NMR (Bruker WP 100) [Fig. 1(a) and (b)]. For PSAF, the protons on the benzene ring appeared at δ = 6.5–8.0 ppm. The methylene group between the two benzene rings was found at δ = 3.5–4.0 ppm, and the other methylene groups —N(CH$_2$)$_3$— were distributed at 1.5–3.5 ppm.[14,15] Molecular weight distributions of PSAF (sodium salts) and DPSAF obtained under different reaction conditions were compared by the GPC method,[16,17] as shown in Figure 2. Two GPC columns (Waters Ultrahy-

drogel-120, 250, with length 30 cm, inner diameter 7.8 mm, and fully porous highly cross-linked hydroxylated polymer as packing material) were combined in series for the measurements. The water (GPC grade) was used as the mobile phase.

Assessment of the Dispersing Abilities of the Condensates

The dispersed clay/water system was prepared using different condensates as dispersants. Table II shows the formulation used in these experiments. For example, the dispersant was dissolved in water (70 g) and mixed with the clay (30 g), then beads (bead no. 50, diameter 10 mm, 160 g) were added for milling. The mixture was milled mechanically by centrifugal ball mills (Retsh) at 600 rpm for 60 min maintained at room temperature. All the prepared pastes were assessed by the following methods:

(a) Rheological Method. Ten milliliters of the dispersed paste was put in the adapter with an SCS-31 spindle, and its viscosity was measured by using a rotating cylindrical viscometer (Brookfield DVII LVT). The apparent viscosities (under a fixed shear rate) were used as a parameter to assess the dispersing ability of the prepared dispersants. All the viscosities were measured at 25°C.

(b) Scanning Electron Microscopy (SEM). The dispersed paste (ca. 1 g) was coated (ca. 25 μm of wet film thickness) on a thin copper plate. After drying (1 day), a small piece of the paste (ca. 4 × 4 mm) was cut and put on an aluminum sheet (with diameter of 20 mm) and electrodeposited with a layer of gold. The surface of the coating film was observed by an SEM electron probe microanalyzer (Hitachi F-4010).
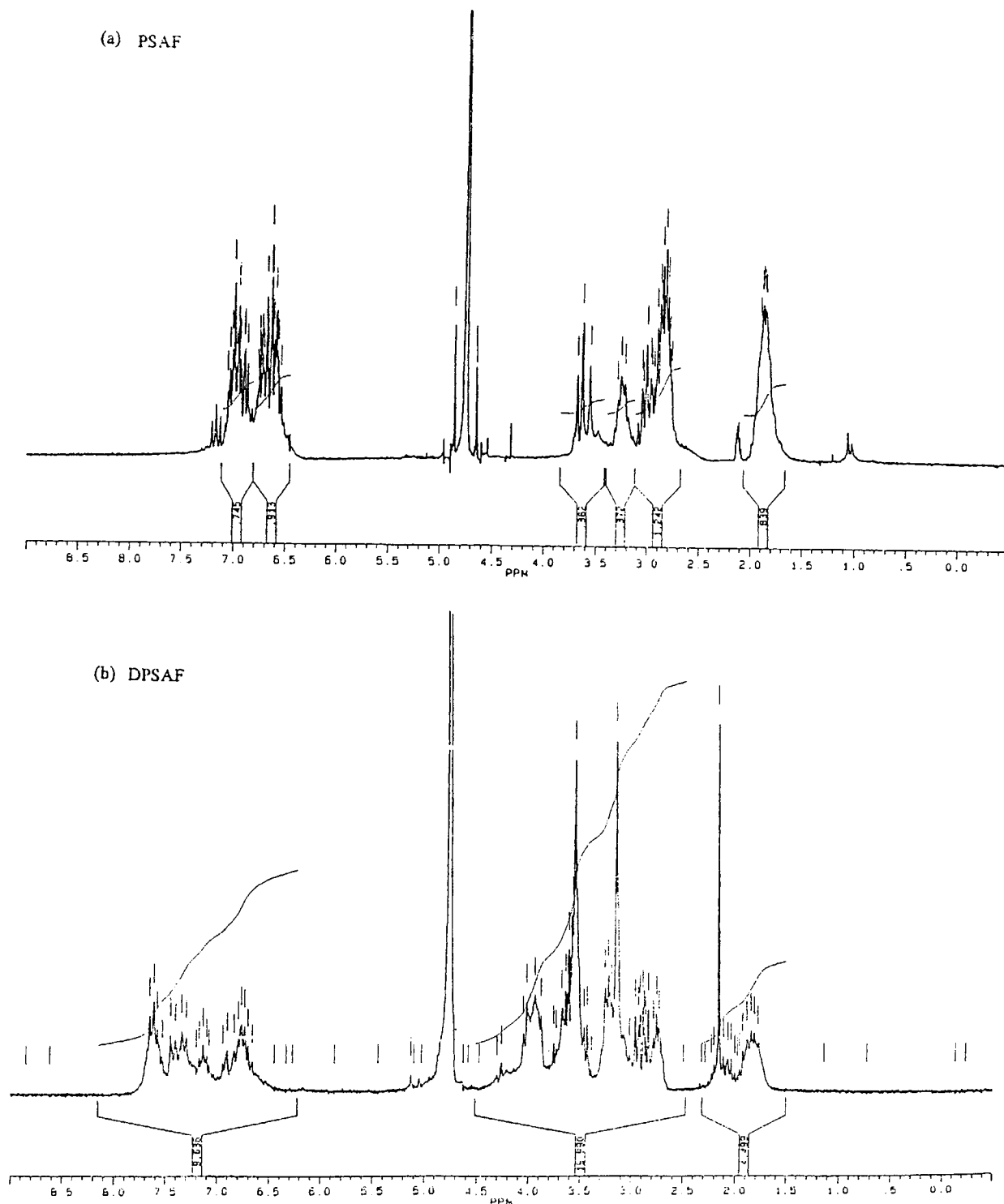
Figure 1 (a) ^{1}H-NMR spectra for PSAF; (b) ^{1}H-NMR spectra for DPSAF.

(c) Sedimentation. The dispersed pastes (ca. 40 mL) were put into 50 mL graduated cylinders and the tops of the cylinders were sealed. The heights of the precipitates were recorded after given time intervals; thus, the rate of precipitation and the final volume ratio were measured.
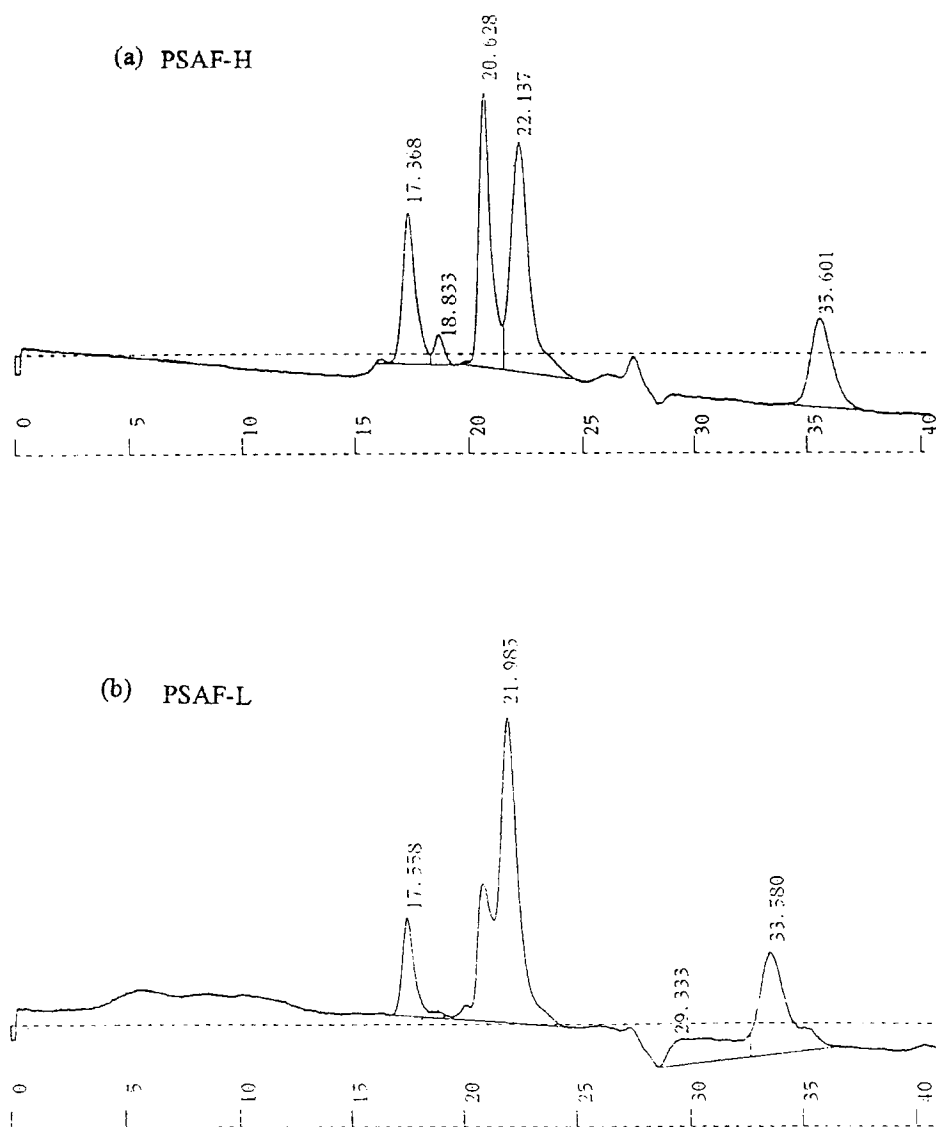
(a) PSAF-H

(b) PSAF-L

Figure 2 (a) GPC spectra for high molecular weight PSAF; (b) GPC spectra for low molecular weight PSAF.

Characterization of the Adsorption of the Condensate

The adsorption of the dispersants onto the surface of the dispersed clay surfaces was measured as fol-

Table II Formulation for Dispersing Clay in Water

Material	Weight (g)
Clay	30
Water	70
Milled ball	160
Dispersant	0–9 wt %

lows. In a 50 mL bottle, 5 g of clay was put into 50 mL of the prepared aqueous solution of the dispersant with different concentrations. After shaking in a thermal bath (25°C, 350 rpm) for 48 h, the suspension was centrifuged (DuPont Sorvall RC-5B) at 15,000 rpm for 60 min at 25°C. The equilibrium concentrations of dispersants in the bulk phase were determined by UV absorption (Jasco 7850) from an absorption calibration curve (Fig. 3).

RESULTS AND DISCUSSION

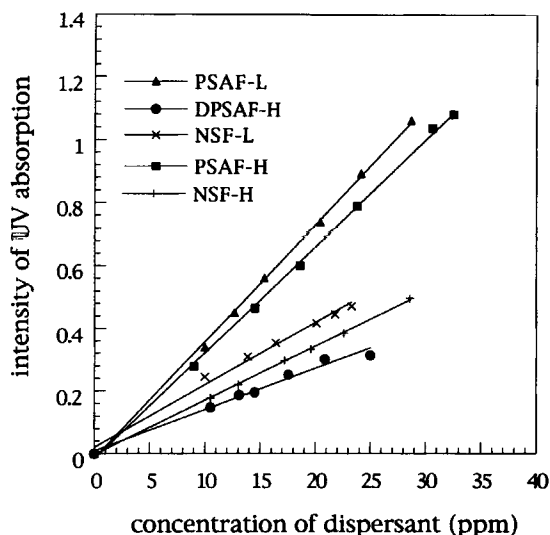NSF were prepared by a sulfonation of naphthalene at 120–160°C, followed by a condensation with

Figure 3 Calibration curve for the intensity of UV absorption as a function of the concentration of dispersant (ppm) for various dispersants (PSAF, NSF, and DPSAF).

formaldehyde (HCHO) at 95-100°C.[7,8] The rate-determining step is the methylenation of naphthalenesulfonate, i.e., the reaction of the protonated HCHO with naphthalenesulfonate.[18] The aniline condensates can be obtained by a similar reaction. However, the amino group of aniline activates the methylenation due to the resonance property of the amino group of aniline; thus, the reaction condition for methylenation is milder, i.e., the reaction temperature is 95-100°C. Also, the sulfonyl group of the title compound is not on the aromatic ring. The sulfonyl group is obtained in the same way as was NSF, i.e., by sulfonation. Therefore, a low concentration of HCl (ca. 0.3 molar ratio of aniline) is used as the catalyst instead of the high concentration of H_2SO_4 (ca. 0.5 molar ratio of naphthalene) to avoid the side reaction of sulfonation on the aromatic ring. The concentration of HCl has to be below a certain level. Above that concentration (pH > 3), HCHO will react with the amino group of aniline instead of methylenation.[19]

The sulfonyl group of the title compound is obtained by the ring-opening reaction of propane sultone. Aniline is a weak base, but the basicity of the amino group of aniline ($k_b = 4.2 \times 10^{-10}$) is strong enough to react with sultone under mild conditions, i.e., the reaction carried out at 70-80°C without acid catalyst.[20]

The formation of condensates can be characterized by NMR as well as by GPC, i.e., both PSAF and DPSAF have the methylene peak at δ = 3.5-4.0 ppm as does NSF[14,15] [Fig. 1(a) and (b)], which

can also be observed for aniline or N,N-dimethylaniline. The appearance of two peaks at δ = 3.5-4.0 ppm means the nonequivalence of the protons in different methylene groups, since, on the benzene ring, the carbon attached to the methylene group can be adjacent to a carbon either substituted by an amino group or not. Meanwhile, the area ratio of the methylene protons to the aromatic protons of the aniline moiety cannot be used to accurately estimate the degree of polymerization of PSAF and DPSAF (n value of PSAF and DPSAF), since the ratio is not remarkably changed with the n value. After the reaction of propane sultone with AF and DAF, the peaks at δ = 2.7-3.4 ppm and δ = 1.7-2.2 ppm appear both for PSAF and DPSAF [Fig. 1(a) and (b)].

Conventional NSF is a condensate with a degree of polymerization of 2-10. Such a low molecular-weight polymer was qualitatively characterized by thin-layer chromatography[9c] or by GPC.[16] For either case, the molecular weight was never calculated, but only the shape of the molecular weight distribution by GPC or the number of spots on the thin-layer chromatography plate was shown. If the molecular weight of NSF is calculated by GPC based on the calibration standards of poly(ethylene oxide), the calculated molecular weight is tremendously high and does not make sense. Figure 2(C)-(D) shows the molecular weight distributions of DPSAF-H and DPSAF-L. Obviously, the area of the peaks appearing at lower elution times is significantly higher for DPSAF-H than for DPSAF-L, e.g., the peak area below 20 min is 21.2% for DPSAF-H compared with
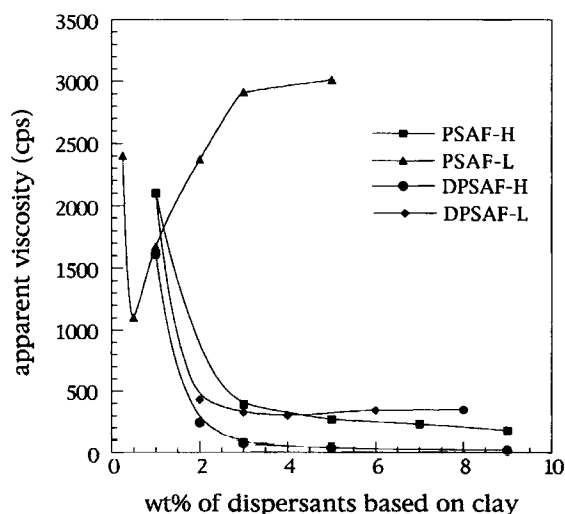

Figure 4 Apparent viscosity (cps) of the dispersed clay as a function of the concentration of dispersants added (wt % based on clay) for PSAF and DPSAF.

12.3% for DPSAF-L. Since the reaction time was longer for DPSAF-H than for DPSAF-L, the longer condensation time increases the degree of polymerization of the condensates. However, if the reaction time is more than 11 h, the DPSAF-H becomes a gel due to the occurrence of cross-linking between the aromatic rings of the DPSAF.

For a dispersing system with high solids content, the shear rate (γ) and the shear stress (τ) have a functional relationship of $\gamma = k\tau^n$.[21,22] On a plot of τ vs. γ for a plastic flow, the intercept and the ap-

parent viscosity (τ/γ) are useful parameters to monitor the extent of dispersion of a system. For a well-dispersed system, the aggregates of particles are small and less associated, and the viscometer spindle senses a smaller hindrance from aggregates at a given shear rate. Consequently, a smaller shear stress and a lower viscosity were detected. In contrast, the agglomerates of a poorly dispersed system form a network that hinders the spindle and results in a higher shear stress and a higher viscosity.[23]
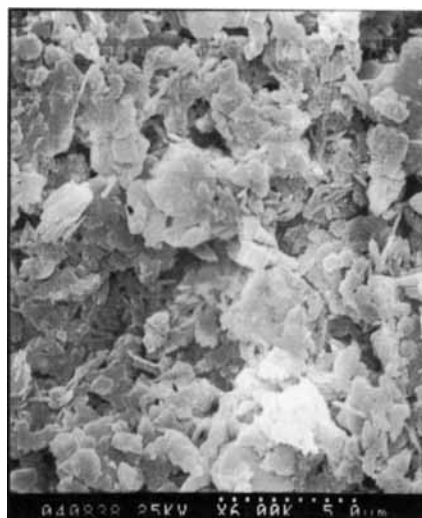
Figure 4 shows the apparent viscosity as a func-
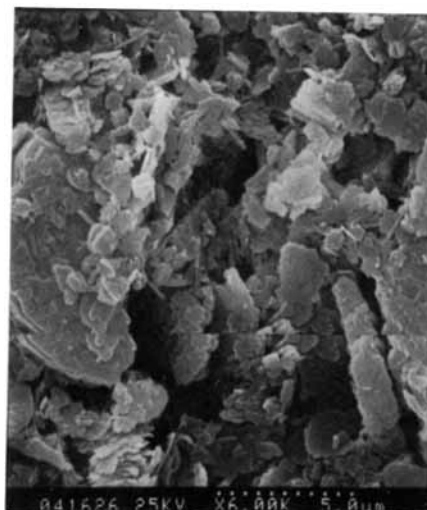

(a) 2%
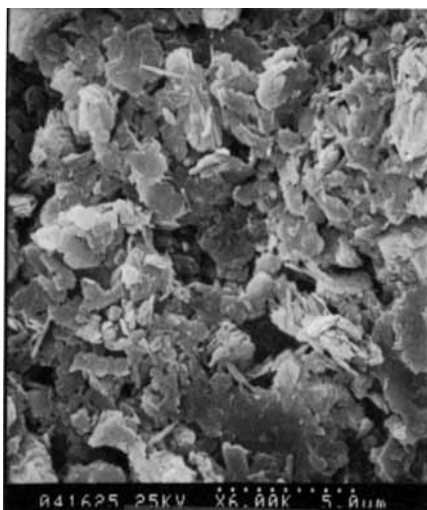
(b) 3%

(c) 9%

Figure 5   SEM micrographs of the clay dispersed in water at different concentrations of DPSAF-H: (a) 2%; (b) 3%; (c) 9%.

tion of dispersant concentration for clay dispersed in water using PSAF and DPSAF as dispersants. At low concentrations of the dispersant, the viscosity decreases as a function of increasing concentration of the dispersant for each plot. There exists a minimum in apparent viscosity (called the minimum viscosity) for PSAF-L; however, the viscosity re-
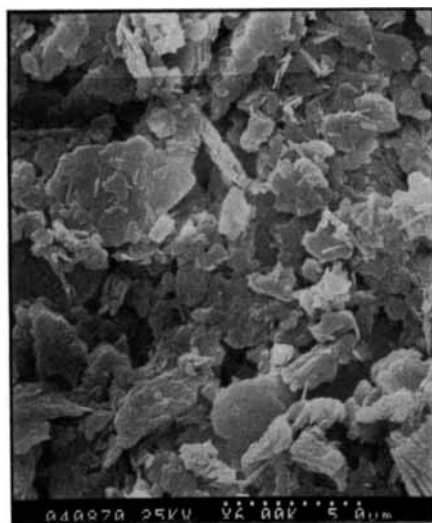
mains constant after the minimum viscosity for PSAF-H, DPSAF-H, and DPSAF-L. The minimum viscosity that PSAF-L can reach (ca. 1100 cps) is remarkably higher than that for PSAF-H, DPSAF-L, and DPSAF-H (ca. 179 cps, 302 cps, and 21.5 cps, respectively). Both for DPSAF and PSAF, the condensate with the higher molecular weight can
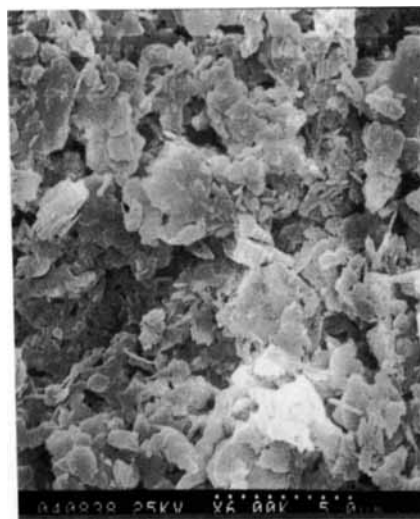
(a) PSAF-L (0.5 wt%)
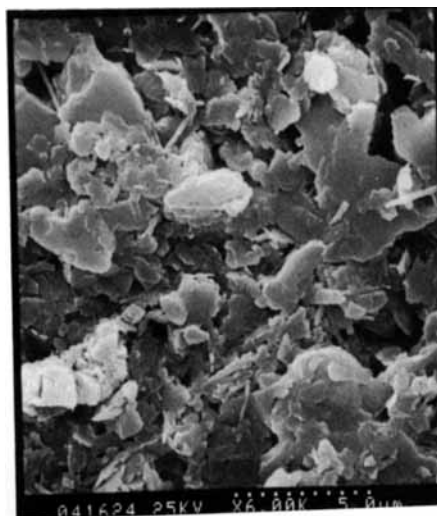
(b) PSAF-H (9 wt%)

(c) DPSAF-L (4 wt%)

(d) DPSAF-H (9 wt%)

Figure 6 SEM micrographs of the clay dispersed in water using dispersants at each optimum concentration: (a) PSAF-L (0.5 wt %); (b) PSAF-H (9 wt %); (c) DPSAF-L (4 wt %); (d) DPSAF-H (9 wt %).

reach a lower minimum viscosity. The concentrations needed for each dispersant to reach its minimum viscosity (called optimum concentration) are ca. 3–5 wt % for DPSAF-L, DPSAF-H, and PSAF-H and 0.5% for PSAF-L. For industrial applications, a good dispersant is expected to reach a low minimum viscosity and to have a low optimum concentration.

SEM can be used to monitor the surface of a film of dispersed particles so that the dispersion state of the particles in solution can be assessed. Figure 5 shows the SEM micrographs (magnification of 6000 times) of the clay dispersed in water using different concentrations of DPSAF-H as dispersants. These concentrations correspond to the points on the curve for DPSAF-H in Figure 4. Obviously, the particles on the plate obtained at the minimum viscosity are more homogeneously dispersed [in Fig. 5(c)] than are the others [in Fig. 5(a) and (b)]. Meanwhile, the pastes that have the minimum viscosities in Figure 4 were coated on a metal plate and the dispersed particles observed by SEM. The results show that the pastes that reach the lower minimum viscosity (DPSAF-H 9.0% and PSAF-H 9.0%) display the more homogeneously dispersed particles (Fig. 6). Comparing the SEM results (Figs. 5 and 6) with the plot of viscosity vs. concentration of dispersants (Fig. 4), it can be concluded that, under comparable conditions, a suspension with a lower viscosity is more homogeneously dispersed.

The dispersing ability of a dispersant for specific particles is related to the effective thickness of the adsorbed layer, which, in turn, is a function of the amount of dispersants adsorbed on the particles and of the orientation of the dispersant in the adsorbed layer.[24,25] To relate apparent viscosity behavior with the adsorption phenomena for PSAF-H and DPSAF-H, the adsorbed amount was measured at different concentrations, as shown in Figure 7. The amount of DSPAF-H adsorbed is significantly higher than that of PSAF-H at low concentrations and reaches a maximum at ca. 3 wt %. This result is in parallel with the trend that the viscosity reaches a minimum and remains constant after 3 wt % (Fig. 4). For PSAF-H, the adsorbed amount increases with increasing concentration (Fig. 7), in parallel to the decreasing trend in viscosity (Fig. 4). Greater adsorption can provide more charges on the surface of the clay, resulting in an increase in the electrostatic repulsion, thus preventing the coagulation of the particles.[1,26]

Clay (kaolinite) is a hydrous aluminum silicate (Al_2O_3—$2SiO_2 \cdot 2H_2O$) with the form of thin platelets. Under normal conditions, the particles carry
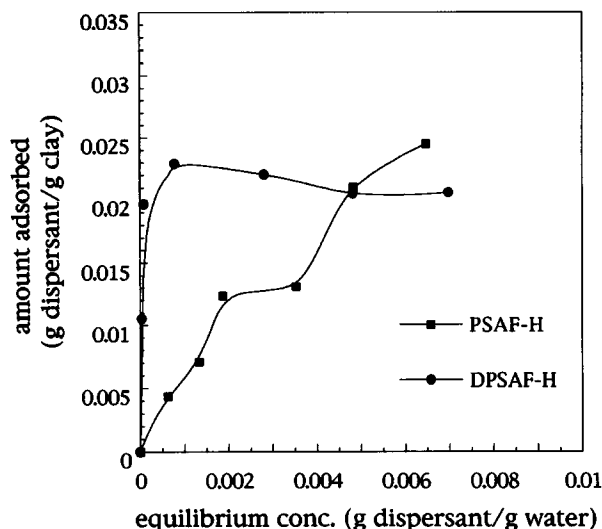

Figure 7 An amount of dispersant adsorbed (g dispersant/g clay) as a function of the equilibrium concentration of dispersants (PSAF-H and DPSAF-H).

negative charges, distributed over the basal surfaces in aqueous suspension; but under acidic conditions (pH 6), alumina exposed at the edges of the plates apparently binds hydrogen ions and assumes a positive charge. However, under alkaline conditions, the edges become neutral or negatively charged.[13] It is interesting to investigate the adsorption of zwitterionic DPSAF-H and anionic PSAF-H on clay influenced by the charges of clay. The measurement in Figure 7 was carried out at a pH of ca. 5. At this pH, the face of the clay is negatively charged and is accompanied by a weak positive charge on the edge. Thus, the zwitterionic DPSAF-H can interact with the clay efficiently due the existence of both positive and negative charges. This explains why the adsorbed amount of DPSAF-H is very high at low concentration. Compared to this, the adsorption of PSAF-H onto clay can be attributed mainly to the interaction between the negatively charged PSAF-H and the weak positive charge on the edge of the clay.

As the pH value increases, the charge on the face of the clay particles is still negative, but the charge on the edge gradually changes from positive to negative. Figure 8 shows the adsorbed amount of DPSAF-H and PSAF-H on the clay as a function of the pH. As the pH increases, the adsorbed amount of the PSAF-H decreases, but that of the DPSAF-H decreases slightly and then increases again to reach a plateau. The decrease in the amount adsorbed for the PSAF-H can be reasonably explained by the increased negative charge of the clay so that
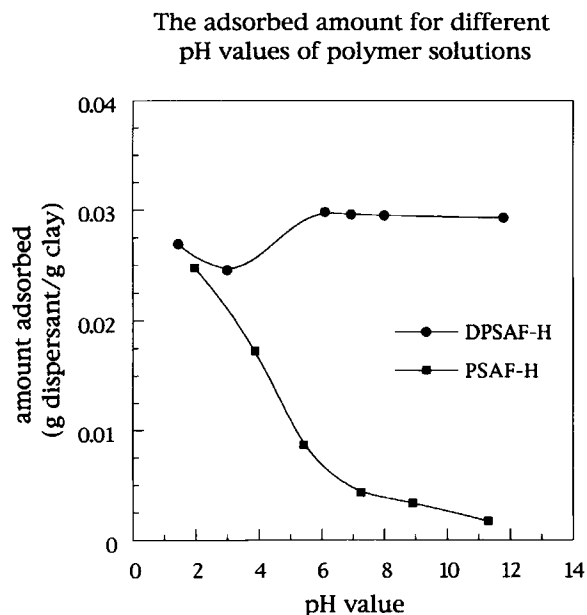
The adsorbed amount for different
pH values of polymer solutions

Figure 8 An amount of dispersant adsorbed (g dispersant/g clay) as a function of the pH of the suspension (PSAF-H and DPSAF-H).

the interaction between the anionic PSAF-H and the clay decreases due to the repulsion. The existence of the plateau for the adsorption of DPSAF-H means that the interaction between the zwitterionic DPSAF-H and clay remains constant above pH 6.

SUMMARY

Compared to the preparation of the naphthalenesulfonate formaldehyde condensate, a milder reaction condition for methylenation (95–100°C) and a low concentration of HCl (ca. 0.3 molar ratio of aniline) was used for synthesizing aniline–formaldehyde condensates. The formation of condensates was characterized by NMR, i.e., both PSAF and DPSAF have the methylene peak at δ = 3.5–4.0 ppm. After the reaction of propane sultone with AF and DAF, the peaks at δ = 2.7–3.4 ppm and δ = 1.7–2.2 ppm appeared both for PSAF and DPSAF, indicating that the propyl sulfonate has been successfully introduced into the condensates. The results from GPC showed that longer condensation times increase the degree of polymerization of the condensates.

The dispersing properties of the condensates were assessed by the viscosity, SEM, and adsorption behaviors. Compared to PSAF, the DPSAF with a higher molecular weight (DPSAF-H) showed sig-

nificantly lower apparent viscosities. Comparing the results of SEM and the viscosity method, it can be concluded that, under comparable conditions, a suspension with a lower viscosity is more homogeneously dispersed. The amount of DPSAF-H adsorbed onto clay was significantly higher than that of PSAF-H at low concentrations of dispersant and reached an optimum after ca. 3 wt %. This result is in parallel with the trend that the viscosity reaches a minimum and remains constant after 3 wt %. For PSAF-H, the adsorbed amount increased with increasing concentration, in parallel with the decreasing trend in viscosity. The zwitterionic DPSAF promotes the dispersing ability of clay in water due to the existence of both positive and negative charges. The decrease in the adsorbed amount for PSAF-H with increasing pH can be explained by the increased negative charge of the clay, so that the interaction between the anionic PSAF-H and clay decreases due to the repulsion.

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