

**CONTROLLING THE DEGREE OF DISPERSION OF ALUMINUM
HYDROXIDE SUSPENSIONS BY ADSORPTION OF IONIC SOLUTES**

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Abstract

The physical properties of amorphous carbonate-containing aluminum hydroxide suspensions can be controlled by adsorption of ionic solutes. A model polyelectrolyte, sodium metaphosphate, and a model anionic surfactant, sodium lauryl sulfate, modified the degree of dispersion regardless of whether the initial

surface potential was positive, neutral or negative. The effect of the ionic solutes could be explained by their effect on the surface potential as described by the point of zero charge and pH relationship.

INTRODUCTION

Many physical properties of aluminum hydroxide suspensions are affected by the surface potential. A series of studies have been reported which demonstrate that adjustment of the surface potential by manipulation of the pH in relationship to the point of zero charge (PZC) is an effective approach for controlling the physical properties of aluminum hydroxide suspensions¹⁻⁹. An alternate approach to adjust the surface potential is the adsorption of an ionic solute¹⁰. The feasibility of this approach was investigated by studying the effect of a model polyelectrolyte, sodium metaphosphate, and a model anionic surfactant, sodium lauryl sulfate, on the degree of dispersion of aluminum hydroxide suspensions having positive, neutral or negative surface potentials.

MATERIALS AND METHODS

An amorphous carbonate-containing aluminum hydroxide suspension was obtained commercially (Chattem Chemical Co.). The equivalent aluminum oxide content was determined by chelatometric titration¹¹. The point of zero charge was found to be 6.8 by potentiometric titration¹. A gasometric displacement technique was

used to determine the carbonate content¹². The use of the fiber optic Doppler anemometer (SIRA) to monitor particle interactions has been previously described⁴. The sediment volume was determined by placing 100 ml of suspension in a stoppered 100 ml graduated cylinder. After undisturbed settling for 7 days at room temperature, the sediment volume was calculated by determining the volume occupied by the sediment and dividing by 100.

The empirical formula, $\text{Al}(\text{OH})_3\text{-R}(\text{HCO}_3)_\text{R}$, was used to calculate the volume fraction, where R is the carbonate to aluminum molar ratio. All suspensions were prepared by dilution with doubly distilled water to a volume fraction of 0.035. The pH of each suspension was adjusted with either 1 N HCl or 1 N NaOH, the appropriate volume of a sodium metaphosphate or sodium lauryl sulfate solution was added and a final dilution with doubly distilled water brought the volume fraction to 0.030.

RESULTS AND DISCUSSION

Three discrete states of dispersion have been identified for suspensions. Repulsive particle interactions predominate in the dispersed state. When the interparticle forces in dispersed suspensions are evaluated by the Derjaguin, Landau, Verwey and Overbeek (DLVO) theory, a strong primary maximum and primary

minimum, but no secondary minimum, are observed. Attractive interparticle forces can lead to aggregation in suspensions. If the aggregates form as a result of a secondary minimum, flocculation occurs. Aggregation occurring in the primary minimum is termed coagulation. The physical properties of suspensions are highly dependent on the degree of aggregation. In order to obtain the desired physical properties for a pharmaceutical suspension, it is frequently necessary to formulate products which are intermediate between the dispersed, flocculated or coagulated states. Thus, techniques are needed to both characterize and adjust the degree of dispersion.

The degree of dispersion of a suspension can be characterized by fiber optic Doppler anemometry (FODA)^{4,5} and sediment volume. FODA measures the shift in frequency of back scattered light caused by randomly moving particles¹³. The area under the curve (AUC) of the modified Lorentzian power spectrum is an indication of the relative number of freely diffusing particles⁴. When the suspension is dispersed, i.e., no particle interactions are occurring, the AUC is at a maximum. However, the AUC approaches zero when the random motion of the particles is impeded by particle interactions. The sediment volume is small when the suspension is dispersed or coagulated and is high when the suspension

is flocculated. Thus, the degree of dispersion can be determined by using the information from these two methods. A dispersed suspension will have a high AUC and a low sediment volume, a flocculated suspension will have a low AUC and a high sediment volume and a coagulated suspension will have a low AUC and a low sediment volume.

The effect of sodium metaphosphate on the degree of dispersion of amorphous carbonate-containing aluminum hydroxide at pH 5.1 is presented in Figure 1. As the PZC was 6.8, the surface potential without the addition of sodium metaphosphate was positive. The control suspension was dispersed as evidenced by the high AUC for the control. The addition of small amounts of sodium metaphosphate caused the AUC to decrease. The AUC approached zero when 0.003 M sodium metaphosphate was added. The AUC increased sharply when 0.005 M sodium metaphosphate was added and remained high as the sodium metaphosphate concentration was increased to 0.010 M.

It was hypothesized that adsorption of small quantities of metaphosphate anion neutralized the positive surface potential. According to the AUC data, the surface potential was neutralized at 0.003 - 0.004 M sodium metaphosphate. Attractive particle interactions predominated in the absence of repulsive electrostatic

interparticle forces and the random motion of the particles was inhibited^{4,5}. Adsorption of additional metaphosphate anions is believed to have caused the surface potential to become negative and dispersion occurred as evidenced by the increase in AUC at 0.005 M sodium metaphosphate.

The effect of sodium metaphosphate on the sediment volume (Fig. 1) supports the hypothesis. The sediment volume increased sharply as the concentration of sodium metaphosphate was increased. The sediment volume increased by a factor of 5.5 at its maximum. It is significant that the maximum sediment volume occurred in the suspension containing 0.003 M sodium metaphosphate and coincided with the minimum AUC. Thus, it was concluded that the suspension was flocculated by the addition of 0.003 M sodium metaphosphate. The sediment volume decreased as the sodium metaphosphate concentration was increased above 0.003 M, reaching the minimum value exhibited by the control. The decrease in sediment volume at higher sodium metaphosphate concentrations and the increased AUC confirms that the suspensions containing greater than 0.005 M sodium metaphosphate were dispersed.

The influence of surface potential¹ upon changes in the physical properties of the suspensions observed in Figure 1 was examined by measuring the point of zero

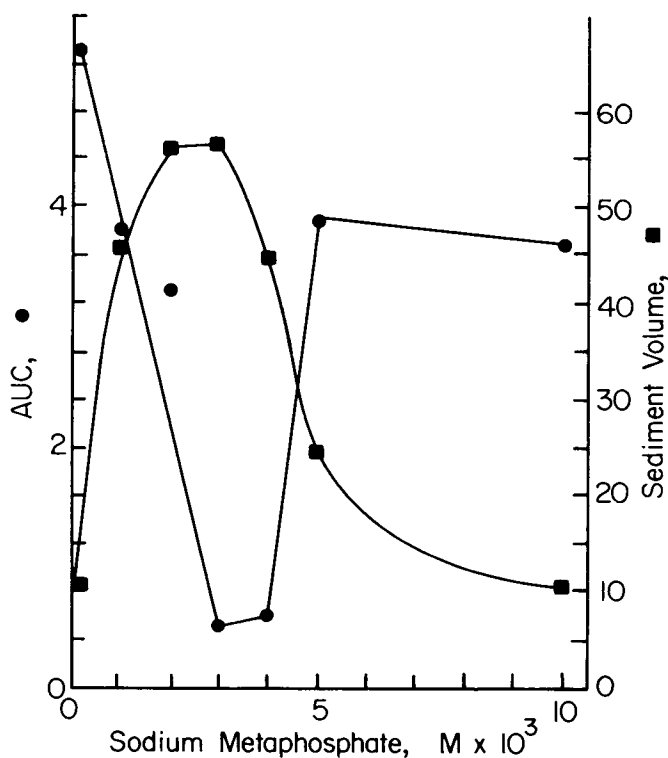


FIGURE 1

Effect of sodium metaphosphate on the degree of dispersion of an amorphous carbonate-containing aluminum hydroxide suspension at a volume fraction of 0.03 and pH 5.1. The degree of dispersion is characterized by the area under the curve (AUC) of the modified Lorentzian power spectrum as determined by fiber optic Doppler anemometry and by the sediment volume which was determined after 7 days of undisturbed sedimentation.

charge (PZC) and pH of the suspensions after the suspensions had aged for 21 weeks at 25°C. The surface potential, calculated by the following equation, is given in Table 1.

$$\text{Surface Potential} = 59.16 \text{ mV (PZC - pH)} \quad \text{Eq. 1}$$

TABLE 1

Effect of Sodium Metaphosphate on the Surface Potential^a of an Amorphous Carbonate-Containing Aluminum Hydroxide Suspension Adjusted to pH 5.1

<u>Sodium Metaphosphate, M x 10³</u>	<u>pH</u>	<u>Point of Zero Charge</u>	<u>Surface Potential, mV^b</u>
0	5.9	7.2	77
1	6.1	6.9	47
2	6.1	7.0	53
3	6.5	7.1	36
4	6.9	7.0	6
5	7.1	6.6	-30
10	7.4	6.0	-83

^aMeasured after aging for 21 weeks at 25°C

^bCalculated by equation 1

Addition of sodium metaphosphate was typically accompanied by a decrease in the point of zero charge and an increase in the pH. The decrease in PZC is consistent with an earlier study which found that the adsorption of phosphate anion by aluminum hydroxide resulted in a decrease in the PZC¹⁴. The increase in pH is probably a reflection of the exchange of surface hydroxide anions for metaphosphate anions. The net effect of adding up to 0.01 M sodium metaphosphate was a change in the surface potential from 77 to -83 mV (Table 1). This change in surface potential from positive to negative is consistent with the changes in AUC and sediment volume presented in Figure 1. It is especially interesting to note that the surface potential approached zero most closely when 0.004 M sodium

metaphosphate was added. This concentration corresponds to the flocculation of the suspension as indicated by the low AUC and high sediment volume. Complete dispersal occurred when the surface potential was -83 mV, i.e., 0.010 M sodium metaphosphate. Thus, the changes in the physical properties of an aluminum hydroxide suspension caused by the addition of a model polyelectrolyte can be explained by the changes in the surface potential calculated from the PZC and pH relationship.

The effect of sodium metaphosphate on the degree of dispersion was also investigated at pH 6.8. As seen in Figure 2, the AUC of the control suspension was low indicating extensive particle interactions. The addition of small quantities of sodium metaphosphate caused the AUC to increase. The maximum AUC was observed in the suspension containing 0.002 M sodium metaphosphate. The sediment volume of the control suspension was high but decreased sharply as small amounts of sodium metaphosphate were added. The sediment volume reached a minimum at 0.003 M sodium metaphosphate. Thus, the control suspension at pH 6.8 appears to be flocculated and the addition of small amounts of metaphosphate anion leads to dispersal.

The behavior seen in Figure 2 can also be explained by the surface potential. The PZC and pH of each suspension was measured after the suspensions had aged

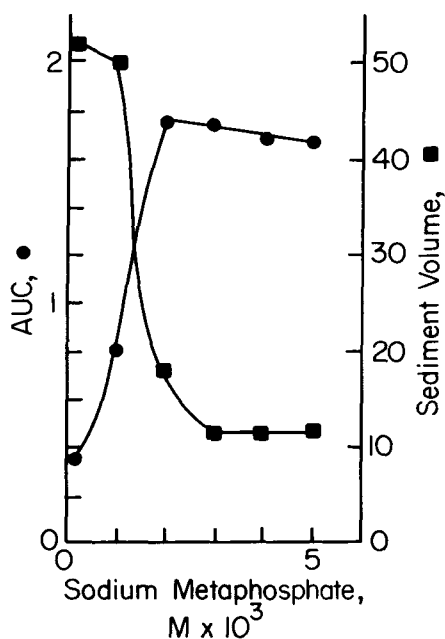


FIGURE 2

Effect of sodium metaphosphate on the degree of dispersion of an amorphous carbonate-containing aluminum hydroxide suspension at a volume fraction of 0.03 and pH 6.8. The degree of dispersion is characterized by the area under the curve (AUC) of the modified Lorentzian power spectrum as determined by fiber optic Doppler anemometry and by the sediment volume which was determined after 7 days of undisturbed sedimentation.

for 21 weeks at 25°C. Application of Equation 1 reveals that the surface potential became increasingly negative as metaphosphate anion was added (Table 2). Dispersal of the suspension occurred when the surface potential reached -77 mV.

The addition of sodium metaphosphate to a suspension having a substantial negative surface

TABLE 2

Effect of Sodium Metaphosphate on the Surface Potential^a of an Amorphous Carbonate-Containing Aluminum Hydroxide Suspension Adjusted to pH 6.8

<u>Sodium</u> <u>Metaphosphate, M x 10³</u>	<u>pH</u>	<u>Point of</u> <u>Zero Charge</u>	<u>Surface</u> <u>Potential, mV^b</u>
0	7.0	6.8	-12
1	7.4	7.0	-24
2	7.8	6.8	-59
3	7.7	6.4	-77
4	7.8	6.5	-77
5	7.7	6.4	-77

^aMeasured after aging for 21 weeks at 25°C

^bCalculated by equation 1

potential was also examined (Fig. 3). Apparently, the surface potential produced by pH adjustment to 8.5 was not adequate to disperse the suspension as the AUC of the control was low and the sediment volume was high. Addition of 0.001 M sodium metaphosphate caused the AUC to increase eight-fold. This was accompanied by a large decrease in the sediment volume. The sediment volume reached a minimum in the presence of 0.002 M sodium metaphosphate. Thus, the suspension at pH 8.5 appeared to be flocculated but was dispersed by the addition of a very small amount of metaphosphate anion.

The surface potential calculated from the PZC and pH measured after 21 weeks at 25°C (Table 3) supports the conclusion drawn from the AUC and sediment volume data presented in Figure 3. The surface potential of

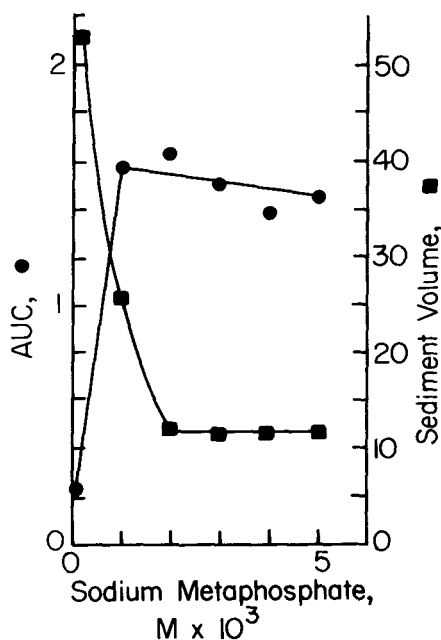


FIGURE 3

Effect of sodium metaphosphate on the degree of dispersion of an amorphous carbonate-containing aluminum hydroxide suspension at a volume fraction of 0.03 and pH 8.5. The degree of dispersion is characterized by the area under the curve (AUC) of the modified Lorentzian power spectrum as determined by fiber optic Doppler anemometry and by the sediment volume which was determined after 7 days of undisturbed sedimentation.

TABLE 3

Effect of Sodium Metaphosphate on the Surface Potential^a of an Amorphous Carbonate-Containing Aluminum Hydroxide Suspension Adjusted to pH 8.5

Sodium Metaphosphate, $M \times 10^3$	pH	Point of Zero Charge	Surface Potential, mV^b
0	7.8	6.6	-71
1	7.9	6.5	-83
2	8.1	6.4	-101
4	8.4	6.3	-124
5	8.1	6.4	-101

^aMeasured after aging for 21 weeks at 25°C

^bCalculated by equation 1

the control was -71 mV which was not large enough to disperse the suspension. Dispersal occurred when the surface potential reached -101 mV, i.e., in the sample containing 0.002 M sodium metaphosphate.

It is interesting to note that a greater surface potential, -101 mV, was required to disperse the suspension which initially had a negative surface potential than was required, -83 mV and -77 mV, to disperse the suspensions with initially positive or neutral surface potentials, respectively. Particle interactions are expected to be symmetrical about the PZC. Thus, the same surface potential, regardless of sign, is expected to be required to disperse a suspension. However, several studies^{1,5,6} have noted that the effect of pH on the physical properties of amorphous carbonate-containing aluminum hydroxide suspensions is not symmetrical about the PZC but that particle interactions are enhanced when the particles are negatively charged. It has been recently hypothesized⁹ that the platy morphology of amorphous carbonate-containing aluminum hydroxide is responsible for the non-symmetric behavior of pH dependent physical properties in relationship to the PZC. Hydrogen bonding between the hydroxide groups on the face of the sheet-like particles and the negatively charged edge groups, which exist when the pH is above the PZC, is believed to

lead to stronger attractive interactions than occur when the edge groups are uncharged. This hypothesis is consistent with the observation that a greater surface potential is needed to disperse the suspension whose initial pH was above the PZC.

The data in Figures 1-3 and Tables 1-3 indicate that the degree of dispersion of amorphous carbonate-containing aluminum hydroxide suspensions can be controlled by the addition of sodium metaphosphate. The effect of the polyelectrolyte can be predicted from the surface potential calculated from the point of zero charge and pH. It should be noted that low concentrations of sodium metaphosphate have profound effects on the physical properties of amorphous carbonate-containing aluminum hydroxide suspensions.

The effect of an anionic surfactant, sodium lauryl sulfate, on the degree of dispersion of amorphous carbonate-containing aluminum hydroxide suspensions was also studied. The suspension adjusted to pH 5.1 was dispersed as evidenced by the high AUC and low sediment volume (Fig. 4). Addition of 0.007 M sodium lauryl sulfate to the suspension produced a sharp decrease in AUC and a sharp increase in sediment volume. The AUC remained low and the sediment volume high when the concentration of sodium lauryl sulfate was 0.007 to 0.020 M. It was concluded that the suspension was

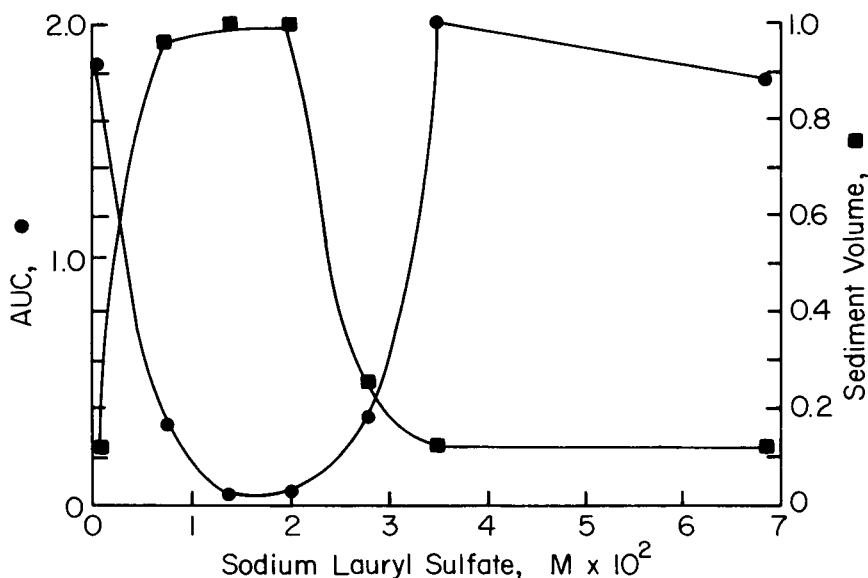


FIGURE 4

Effect of sodium lauryl sulfate on the degree of dispersion of an amorphous carbonate-containing aluminum hydroxide suspension at a volume fraction of 0.03 and pH 5.1. The degree of dispersion is characterized by the area under the curve (AUC) of the modified Lorentzian power spectrum as determined by fiber optic Doppler anemometry and by the sediment volume which was determined after 7 days of undisturbed sedimentation.

flocculated in this range. Concentrations of sodium lauryl sulfate greater than 0.035 M caused the suspension to be dispersed as the AUC reached a maximum and the sediment volume reached a minimum.

The addition of sodium lauryl sulfate produced an increase in the pH and a decrease in the point of zero charge as was observed when sodium metaphosphate was studied. The result of the changes in PZC and pH on the

Table 4

Effect of Sodium Lauryl Sulfate on the Surface Potential^a of an Amorphous Carbonate-Containing Aluminum Hydroxide Suspension Adjusted to pH 5.1

<u>Sodium</u> <u>Lauryl Sulfate, M x 10²</u>	<u>pH</u>	<u>Point of</u> <u>Zero Charge</u>	<u>Surface</u> <u>Potential, mV^b</u>
0	6.0	6.9	53
0.7	6.1	6.9	47
1.4	6.5	6.5	0
2.0	6.8	6.3	-14
2.8	6.9	6.4	-30
3.5	7.1	6.3	-47
6.9	7.4	5.3	-125

^aMeasured after aging for 46 weeks at 25°C

^bCalculated by equation 1

surface potential calculated by Equation 1 is presented in Table 4.

The surface potential of the control was positive because the pH was below the PZC. Addition of lauryl sulfate anion led to a reduction of the positive surface potential which reached zero at 0.014 M. Comparing the surface potential to Figure 4, it is concluded that the suspension was flocculated when the surface potential was between 47 and -14 mV. Dispersal occurred when the surface potential reached -47 mV.

The low AUC and high sediment volume suggests that the suspension was flocculated when the pH was adjusted to 6.8, i.e., the PZC (Fig. 5). The addition of a small amount of the anionic surfactant (0.007 M) produced a higher sediment volume but no change in the AUC,

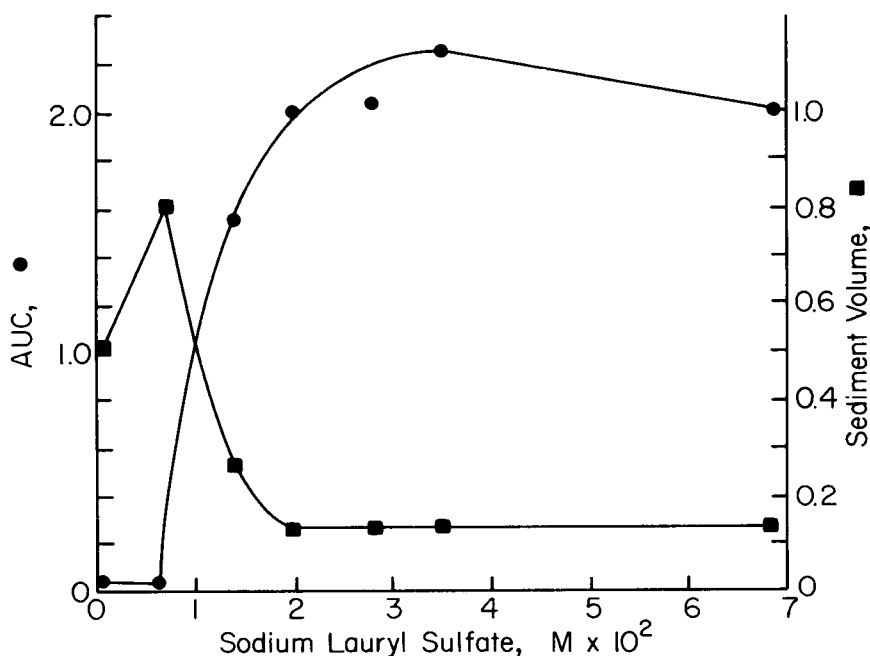


FIGURE 5

Effect of sodium lauryl sulfate on the degree of dispersion of an amorphous carbonate-containing aluminum hydroxide suspension at a volume fraction of 0.03 and pH 6.8. The degree of dispersion is characterized by the area under the curve (AUC) of the modified Lorentzian power spectrum as determined by fiber optic Doppler anemometry and by the sediment volume which was determined after 7 days of undisturbed sedimentation.

suggesting increased flocculation. The addition of 0.014 M sodium lauryl sulfate produced an increase in the AUC and a decrease in sediment volume. Higher concentrations of sodium lauryl sulfate continued this trend until complete dispersion was achieved at 0.020 M sodium lauryl sulfate.

Table 5

Effect of Sodium Lauryl Sulfate on the Surface Potential^a of an Amorphous Carbonate-Containing Aluminum Hydroxide Suspension Adjusted to pH 6.8

<u>Sodium</u> <u>Lauryl Sulfate, M x 10²</u>	<u>pH</u>	<u>Point of</u> <u>Zero Charge</u>	<u>Surface</u> <u>Potential, mV^b</u>
0	7.0	6.8	-12
0.7	7.0	6.8	-12
1.4	6.9	6.3	-36
2.0	7.2	6.6	-36
2.8	7.0	6.0	-59
3.5	7.4	6.0	-83
6.9	7.6	4.4	-189

^aMeasured after aging for 46 weeks at 25°C

^bCalculated by equation 1

The effect of sodium lauryl sulfate on the surface potential of the suspension adjusted to pH 6.8 is presented in Table 5. The surface potential became increasingly negative as the concentration of sodium lauryl sulfate was increased. Comparison with Figure 5 suggests that a surface potential of -36 mV is required to disperse the suspension.

The addition of sodium lauryl sulfate to suspensions having a negative surface potential, i.e., pH > PZC, leads to dispersion. As seen in Figure 6, the control suspension appeared to be flocculated as the AUC was low and the sediment volume was high. Addition of 0.007 M sodium lauryl sulfate appeared to enhance the flocculation as the sediment volume increased from 0.55 to 0.63 while the AUC remained low. Addition of greater

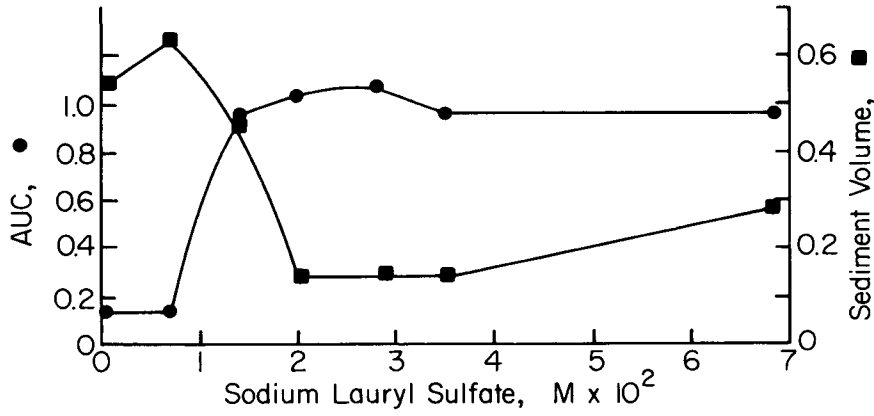


FIGURE 6

Effect of sodium lauryl sulfate on the degree of dispersion of an amorphous carbonate-containing aluminum hydroxide suspension at a volume fraction of 0.03 and pH 8.5. The degree of dispersion is characterized by the area under the curve (AUC) of the modified Lorentzian power spectrum as determined by fiber optic Doppler anemometry and by the sediment volume which was determined after 7 days of undisturbed sedimentation.

Table 6

Effect of Sodium Lauryl Sulfate on the Surface Potential^a of an Amorphous Carbonate-Containing Aluminum Hydroxide Suspension Adjusted to pH 8.5

Sodium Lauryl Sulfate, $M \times 10^2$	pH	Point of Zero Charge	Surface Potential, mV^b
0	6.8	7.2	24
0.7	7.4	6.6	-47
1.4	7.4	6.3	-65
2.0	7.5	6.1	-83
2.8	7.6	5.8	-107
3.5	7.6	5.7	-112
6.9	7.6	5.6	-118

^aMeasured after aging for 34 weeks at 25°C

^bCalculated by equation 1

than 0.014 M sodium lauryl sulfate produced an increase in AUC and a decrease in sediment volume.

The surface potential calculated from the PZC and pH values are consistent with the results shown in Figure 6. The surface potential became increasingly negative as the concentration of sodium lauryl sulfate was increased (Table 6). Thus, dispersion occurred at surface potentials greater than -65 mV.

In the experiments with sodium lauryl sulfate it was noted that a greater surface potential was required to disperse the suspension when the initial pH was above the PZC, -65 mV, than was required when the initial pH was below or equal to the PZC, -47 or -36 mV, respectively. This asymmetrical behavior was also observed in the sodium metaphosphate experiments. The hypothesis to explain this behavior is the same as offered for the sodium metaphosphate experiments.

ACKNOWLEDGMENTS

This report is Journal Paper No. 10,100, Agricultural Experiment Station, Purdue University, West Lafayette, Indiana 47907.

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