

Microelectrophoresis and Electron-Microscope Studies with Polymeric Flocculants*

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Synopsis

Mechanisms for the stabilization and flocculation of colloids have been indicated by microelectrophoresis measurements and electron-microscope observations with model colloids and polymeric flocculants. Zeta-potential (ζ) changes and details of floc structure were observed with silica and polystyrene latex colloids. Bridging fibers of polyamine-type flocculants appear to extend radially from the colloidal particles and vary in thickness from 20 to 300 Å. Charge neutralization and bridging may function simultaneously. Incremental additions of cationic flocculants produce gradual reduction in the negative ζ , and maximum flocculation is observed near zero ζ . Subsequent addition of flocculant reverses the potential and finally effects redispersion of the colloid. If incipient charge reversal is produced with a relatively low molecular weight cationic polymer, large flocs may then be formed on the addition of a high molecular weight anionic flocculant. Direct addition of an anionic polymeric flocculant to a negatively charged colloid may raise the negative ζ to a surprisingly high value and may thus effect stabilization instead of flocculation of the colloid.

INTRODUCTION

In addition to our studies on the removal of surface contaminants from refinery effluent water,¹⁻³ we have focused considerable attention on the flocculation of colloidal contaminants.⁴ Such colloids, both organic and inorganic, pose serious problems in water purification. Even in low concentrations, they cause turbidity, tend to adsorb objectionable taste and odor components, and usually interfere with purification processes that involve membranes or adsorbents.⁵⁻⁷ In general, colloidal contaminants must be flocculated before they can be removed by flotation, filtration, sedimentation, or other conventional methods of water treatment.

Despite extensive studies on the stabilization and destabilization of colloids and emulsions, there are still many unexplained phenomena in this complex field.⁸⁻¹⁴ Most investigators believe, however, that the stability of colloidal systems is related to the electrical charge carried by the colloidal particles and that many flocculating agents are effective insofar as they are able to reduce or neutralize this charge.

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Recent work in other laboratories has demonstrated charge neutralization effects in many systems and in addition has suggested bridging with polymeric flocculants. The particle size of a colloidal latex has been related to the optimum concentration of a relatively low molecular weight commercial cationic flocculant in turbidity and electrophoresis studies.¹⁵ Experiments with colloidal minerals and high molecular weight polymers of varying lengths strongly suggest bridging.¹⁶ A similar conclusion has been drawn from a study of colloidal silica with polyethylenimines of varying molecular weights¹⁷ and with poly(1,2-dimethyl-5-vinylpyridinium methyl sulfate).¹⁸ High molecular weight anionic polymers in the presence of inorganic cations may be effective flocculants for negative inorganic sols such as silver halides.^{13,19} Similar studies with latex colloids substituted for the silver halides present interpretation problems.¹⁴ Arguments for polymeric bridging have been advanced in related flocculation studies with high molecular weight polymers.²⁰⁻²³ More direct evidence to support (or disprove) bridging in relatively simple systems was thus sought in the present study.

In a continuation of our work to determine the mechanism of flocculation, we are using both electron microscopy and electrophoresis to observe the effects of polymeric flocculating agents on model colloidal systems. Because electrophoresis measurements on a wide variety of refinery and related effluent water samples have indicated that essentially all the colloidal contaminants, both organic and inorganic, have a negative charge or zeta potential (ζ), we have chosen negatively charged colloids as our model systems—silica as the inorganic and polystyrene latex as the organic colloid. Both types of material have a relatively uniform particle size, a high ζ , and a consistent behavior.

TABLE I
Polymeric Flocculants

| Designation | Type | Description | Molecular weight, M_w | Supplier |
|-------------|----------|---|-------------------------|-------------|
| C-7 | cationic | water-soluble bisulfate salt of the homopolymer of 2-vinylimidazole | 1.0×10^6 | Rohm & Haas |
| C-3 | cationic | condensation polymer of a polyalkylene-polyamine and an epihalohydrin | 1.3×10^4 | Rohm & Haas |
| Montrek 18 | cationic | polyethylenimine | 2.1×10^3 | Dow |
| Cat-Floc | cationic | linear homopolymer of diallyldimethylammonium chloride | 2.0×10^6 | Calgon |
| A-22 | anionic | polyacrylamide with negative acrylate groups | 3.0×10^6 | Dow |

Organic polymers are under study as flocculants in preference to inorganic salts because: (1) smaller amounts are needed (handling facilitated); (2) they may be burned off (removal problem reduced); (3) they are relatively insensitive to and have little effect on pH; (4) they may function by both charge neutralization and bridging; (5) they form stable, low-density flocs (flotation facilitated). In general, we start with a pure model colloid of known concentration and particle size, add measured amounts of a flocculant, and observe any resultant changes in ζ and in the appearance of the colloid and the flocs.

Our most recent experiments, described herein, provide further support for charge neutralization and bridging mechanisms in flocculation. Changes in the stability of a colloid depend on both the type and concentration of the flocculant. Whereas cationic agents generally act as charge neutralizers, and therefore as destabilizers, the anionic agents tend to stabilize rather than flocculate negatively charged colloids.

EXPERIMENTAL

Materials

The model colloidal dispersions were prepared from:

1. Minusil #5 (Pennsylvania Glass Sand Corporation), a finely divided silica with a ζ of about -30 mV and an average particle size of about 1μ .
2. LS-040-A, LS-1132-B, and LS-052-A (Dow Chemical Company), polystyrene latices with a ζ of about -50 mV and particle diameters of 880, 910, and 1260 \AA , respectively.

The dispersing medium was water twice distilled from quartz and stored in quartz flasks.

The flocculants are described in Table I. They are commercial-type products provided by the indicated manufacturers and were used as received. Weight-average molecular weights (M_w) were measured by sedimentation equilibrium at 25°C on a Spinco Model E ultracentrifuge. Infrared characterization of the flocculants was consistent with the structures indicated in Table I.

Apparatus and Procedure

Electrophoretic mobilities and specific conductivities were measured on a Zeta-Meter apparatus.²⁴⁻²⁶ Particle velocities were determined in two directions by reversing polarity; at least ten particles were measured in each direction. The ζ values were calculated from the particle velocities by means of the Helmholtz-Smoluchowski equation:

$$\zeta = 4\pi\mu\eta/D$$

where μ is the electrophoretic mobility and η and D are, respectively, the viscosity and the dielectric constant of the liquid. Although many assumptions are involved in such a calculation,²⁷ the *relative* values, whether ex-

pressed as electrophoretic mobilities or zeta potentials, are meaningful and useful. Reproducibility of ζ is quite satisfactory for these systems (generally ± 2 mV), whereas the specific conductivities, particularly in the low range, are somewhat scattered. Mobilities were measured about 20 min after the appropriate flocculant addition had been made to 100 cc of the colloidal dispersion and the combined system had been gently agitated for 5 min.

Particle size and flocculant bridging studies were performed on an RCA-type EMU electron microscope. The samples, which were the same as those studied in the microelectrophoresis experiments, were deposited directly on collodion supports and shadow-cast with a gold-palladium alloy at an angle of about 15 degrees. Some samples were freeze dried at -78° and at -195°C .

"Equivalent monolayers" (area flocculant/area colloid) were estimated as follows: The surface area of the horizontally oriented polymer was assumed to be $1000\text{ m}^2/\text{g}$ on the basis of extensive previous work with polar polymers,²⁸⁻³¹ and the surface area of the colloidal particles was obtained from particle size measurements with the electron microscope. Adsorption of the polymer was considered essentially complete, an assumption supported by the relatively small change in specific conductivity that occurred with moderate additions of the flocculant.^{12, 20} Minimum coiling and folding of the polymer at the solid-liquid interface are assumed. In a given series, the "equivalent monolayers" give a number directly proportional to the ppm of flocculant and should eventually facilitate interpretation of these data.

The appearance of the colloid and flocs was judged from a combination of observations with the Zeta-Meter, the Hach Turbidimeter, and the naked eye.

RESULTS AND DISCUSSION

The effects of some representative polymeric flocculants on the ζ and flocculation behavior of the two model colloids are summarized in Tables II and III. In both types of colloids, an increasing concentration of a cationic flocculant causes the ζ to change from negative to positive. At about 0.1 to 0.4 monolayer, the ζ approaches zero and flocculation becomes evident. With excess flocculant, ζ levels off or decreases slightly and the colloid tends to redisperse. By contrast, an increasing concentration of the anionic flocculant causes ζ to become more negative, and no flocculation occurs.

Electrophoresis of the silica colloid shows that most of the particles slow down or stop moving as the concentration of the cationics reaches 0.4 monolayer. The approach to zero ζ in this region suggests that considerably less than half of the silica surface is composed of negatively charged sites. Greater separation of positively charged groups on the polymer and the formation of loops or folds in the adsorbed polymer chains would

TABLE II
Effect of Polymeric Flocculants on the Zeta Potential of Colloidal Silica^a

| Flocculant concentration ppm | Equivalent monolayers ^b | Specific conductivity, $\mu\text{mhos/cm}$ | Zeta potential, mV |
|---------------------------------------|---------------------------------------|--|--------------------------|
| <i>Rohm & Haas C-7 (Cationic)</i> | | | |
| 0.0 | 0.0 | 3 | -27 |
| 0.01 | 0.05 | 14 | -29 |
| 0.05 | 0.3 | 10 | -11 |
| 0.075 | 0.4 | 6 | 0 |
| 0.10 | 0.5 | 10 | +9 |
| 1.0 | 5.0 | 12 | +26 |
| 10 | 50 | 37 | +28 |
| 50 | 250 | 190 | +26 |
| 100 | 500 | 370 | +26 |
| <i>Dow Montrek 18 (Cationic)</i> | | | |
| 0.0 | 0.0 | 4 | -30 |
| 0.01 | 0.05 | 7 | -30 |
| 0.05 | 0.3 | 14 | -5 |
| 0.075 | 0.4 | 4 | +37 |
| 0.10 | 0.5 | 3 | +35 |
| 1.0 | 5.0 | 4 | +42 |
| 10 | 50 | 7 | +42 |
| 50 | 250 | 20 | +24 |
| 100 | 500 | 31 | +21 |
| <i>Dow A-22 (Anionic)</i> | | | |
| 0.0 | — | 4 | -30 |
| 0.01 | — | 4 | -37 |
| 0.1 | — | 3 | -40 |
| 1.0 | — | 3 | -53 |
| 10 | — | 22 | -68 |
| 100 | — | 96 | -78 |

^a 100 ppm Minusil #5.

^b Area flocculant/area colloid.

give less coverage. The plateau in ζ above five monolayers may indicate adsorption equilibrium. However, if adsorption continues, thickness of the flocculant film does not appreciably change ζ . A subsequent decrease in ζ at high concentrations may indicate that a mass or viscosity effect is reducing mobility; an increase in specific conductivity suggests ion compression of the double layer.

The electron micrographs in Figure 1 indicate how flocculation may occur. For example, Figure 1A shows the original colloidal silica in separate and distinct particles averaging about 1μ and no flocs of any significance. In sharp contrast, Figure 1B shows that samples with 0.4 monolayer of C-7 give large tightly packed flocs but essentially no individual particles of the original silica.

TABLE III
Effect of Polymeric Flocculants on the Zeta Potential of Polystyrene Latices

| Flocculant concentration ppm | Equivalent monolayers* | Specific conductivity, $\mu\text{mhos/cm}$ | Zeta potential, mV | Appearance |
|--|---------------------------|--|--------------------------|------------------------------|
| <i>Dow LS-040-A Latex (270 ppm); Rohm & Haas C-7 (Cationic)</i> | | | | |
| 0.0 | 0.0 | 20 | -52 | slightly turbid |
| 0.01 | 0.0006 | 26 | -53 | no change |
| 0.1 | 0.006 | 25 | -46 | no change |
| 1.0 | 0.06 | 31 | -32 | no change |
| 3.0 | 0.19 | 21 | -25 | turbid (flocs) |
| 4.0 | 0.25 | 26 | -20 | turbid (many flocs) |
| 5.0 | 0.30 | 30 | -11 | turbid (all flocs) |
| 6.0 | 0.40 | 32 | +24 | slightly turbid (many flocs) |
| 8.0 | 0.50 | 37 | +31 | slightly turbid (flocs) |
| 10 | 0.60 | 44 | +33 | no change |
| <i>Dow LS-040-A Latex (150 ppm); Calgon Cat-Floc 04L7A1 (Cationic)</i> | | | | |
| 0.0 | 0.0 | 6 | -46 | slightly turbid |
| 0.02 | 0.002 | 6 | -46 | no change |
| 0.2 | 0.02 | 6 | -44 | no change |
| 0.4 | 0.04 | 8 | -33 | no change |
| 0.6 | 0.06 | 9 | -24 | turbid |
| 1.0 | 0.1 | 13 | -17 | turbid (flocs) |
| 1.2 | 0.12 | 15 | +12 | very turbid (flocs) |
| 2.0 | 0.2 | 15 | +22 | turbid (flocs) |
| 10 | 1.0 | 9 | +35 | slightly turbid (no flocs) |
| <i>Dow LS-1132-B Latex; Dow A-22 (Anionic)</i> | | | | |
| 0.0 | — | 3 | -38 | slightly turbid |
| 0.1 | — | 4 | -38 | no change |
| 1.0 | — | 5 | -46 | no change |
| 10 | — | 10 | -63 | no change |
| 30 | — | 24 | -73 | no change |
| 50 | — | 32 | -74 | no change |

* Area flocculant/area colloid.

Figures 1C and 1D are shadow-cast samples of the flocs at two different magnifications, where the shadows appear as light areas (direction of shadow-casting is indicated by arrows). Shadow casting is important because thin fibers of polymer would be transparent to the electron beam. Tight packing is again apparent. But the most striking features are the thread-like or fiber-like structures extending radially from some of the particle surfaces. Presumably these represent polymeric flocculant that, in reaching out, captures and binds neighboring particles. Moreover, bridging between particles is clearly indicated.

At the greater magnification in Figure 1D, the shadow widths indicate that some fibers are 200 to 300 Å, whereas others appear to be 20 to 30 Å in diameter. The latter values approach the expected diameter for a single

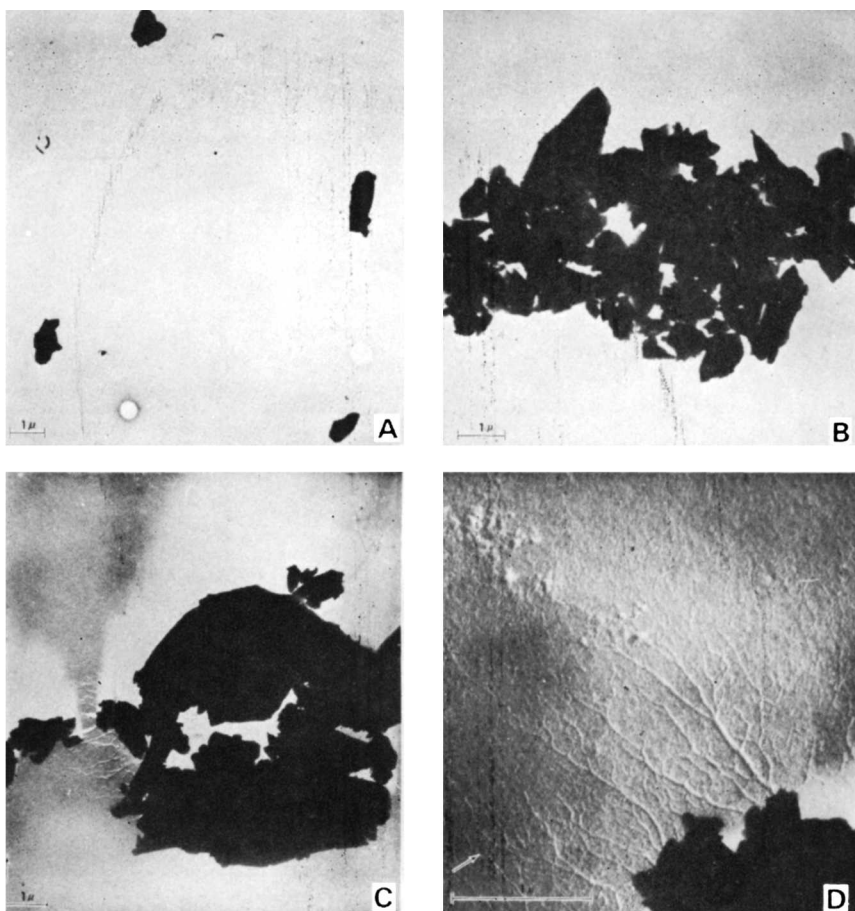


Fig. 1. Electron micrographs of colloidal silica and a cationic polymeric flocculant (C-7): (A) silica blank; (B) silica plus flocculant; (C) silica plus flocculant (shadow cast); (D) silica plus flocculant at higher magnification (shadowcast).

polymer chain with some branching or perhaps some coiling or folding. Thickness of the radially oriented fibers decreases with distance from the silica surface. Fiber formation clearly lessens the material available for thin-film adsorption.

Some samples to which a great excess of flocculant has been added (500 equivalent monolayers) show particles that appear to have an outer shell or layer of material that is almost transparent to the electron beam. These outer layers may well be the adsorbed polymer. No flocs are observed in the latter samples; redispersion has been effected.

As shown in Figures 2 and 3, there is also bridging between latex particles (1260 Å) in the presence of an excess of C-7 flocculant, and the fibrous structures resemble those found with silica. The shadows again indicate that fiber thickness covers a broad range, 20 to 300 Å. Not only do all of the

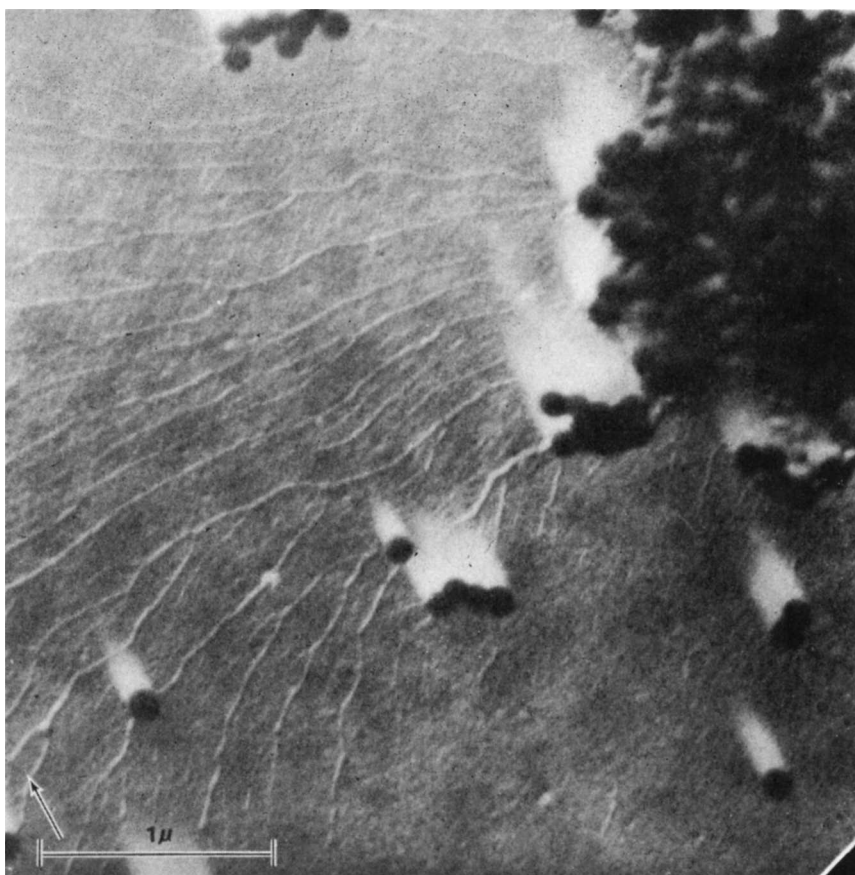


Fig. 2. Electron micrograph of polystyrene latex (LS-O52-A) and a cationic polymeric flocculant (C-7).

latex particles in Figure 3 appear to be attached to fibers (none is in the "open" area), but apparently they are attracted to the thicker portions of the fibers and, in many cases, to the points of branching. Electrical attraction plus van der Waals forces are undoubtedly responsible for such attachments.

Because of the many inherent difficulties in sample preparation and electron microscopy proper,²⁸ a one-to-one correspondence between the micrographs and the original system cannot be claimed. However, changes observed in the micrographs undoubtedly parallel changes that occur in the original system; moreover, many micrographs may in fact give true pictures of the original system. In spite of surface tension forces that may pull together the polymer molecules on evaporation of the dispersing medium, extremely fine fibers are observed in the micrographs. These fibers approach the thickness of single polymer molecules and suggest that still smaller fibers beyond the resolution of our instrument may well be present,

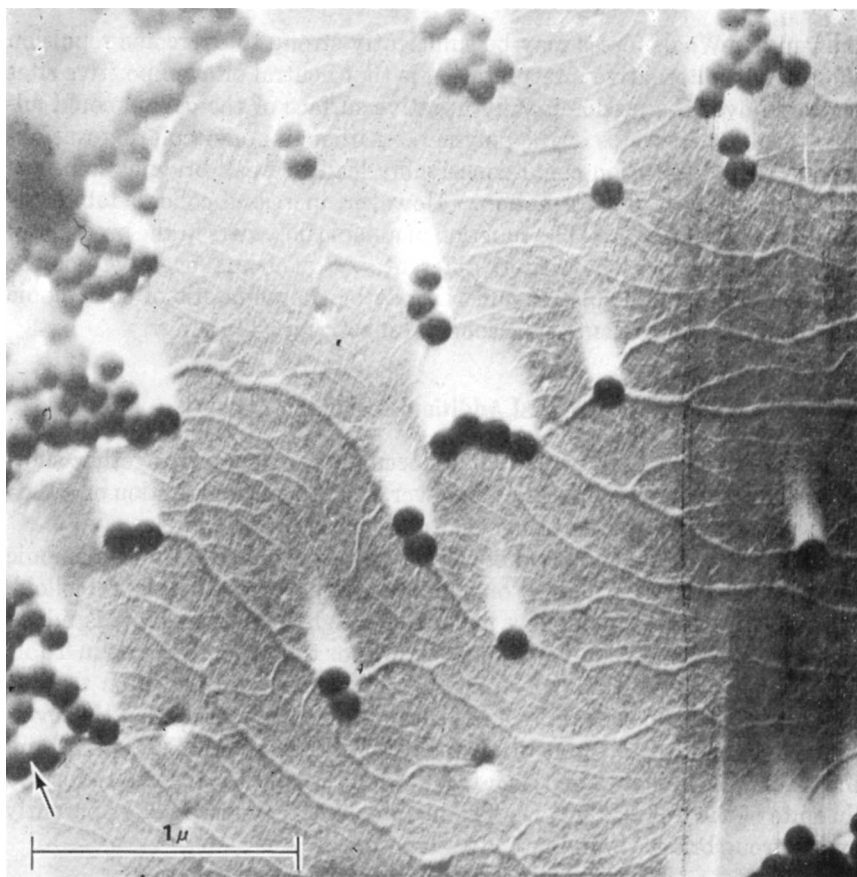


Fig. 3. Electron micrograph of polystyrene latex (LS-052-A) and a cationic polymeric flocculant (C-7).

particularly in the branched structures shown in Figures 1D, 2, and 3. Moreover, it is significant that no matrix structures of fine polymer fibers are observed in the absence of the colloidal particles (silica or latex).

Several different techniques of sample preparation have shown bridges some of which are ribbon-like in structure. However, freeze drying, which minimizes surface tension effects but introduces other difficulties, has thus far shown only relatively gross connecting structures. At present, it appears difficult to devise any technique—other than electron microscopy—that will unequivocally establish or disprove polymeric bridging. Certainly the micrographs strongly suggest the presence of bridging structures in the original system. Related studies with widely different systems indicate similar structures.^{32,33}

The increase in negative ζ observed with an anionic flocculant, A-22 (Tables II and III), indicates that the polymer is adsorbed by the colloidal particles in spite of the similar charges of the two components. Possibly

the van der Waals forces may be sufficiently strong to overcome repulsion effects. An alternative interpretation is that neutral or even positive sites scattered over the predominately negative surface of the colloid could adsorb the anionic groups of the polymer. Although no flocculation was observed, such adsorption could conceivably lead to weak bridging and perhaps eventually to floc formation. However, increased colloid stability is the more logical result. The function of anionic polymers in the presence of inorganic cations may be entirely different.^{13,19} The final negative ζ on the addition of A-22 in Tables II and III may be characteristic of the anionic polymer and independent of the colloidal substrate.

Sequential Addition of Flocculants

We have found that two cationic flocculants introduced together show only slight synergistic effects. However, the sequential addition of a cationic and an anionic polymer gives rather remarkable results.

Table IV contrasts the effect of adding first a cationic and then an anionic polymer with that of adding only a cationic polymer to a latex colloid. When C-3, a highly polar low molecular weight cationic agent, is added alone, the results are similar to those shown for the cationic agents in Table III. That is, flocs begin to form as ζ approaches zero and then tend to break up as the concentration of the cationic polymer increases. However, when C-3 is added to the point of incipient charge reversal (1.9 ppm) and then A-22, the anionic agent, is introduced, unusually large flocs are formed (in spite of the ζ of -22 mV). The high molecular weight A-22 apparently forms strong bridges in the extended structures.

TABLE IV
Effect of the Sequential Addition of a Cationic and an Anionic
Flocculant on the Zeta Potential and Flocculation of Polystyrene Latex^a

| Flocculant concentration, ppm | | Specific conduc- tivity, μ hos/cm | Zeta po- tential, mV | Appearance |
|----------------------------------|------|--|-------------------------------|---|
| C-3 | A-22 | | | |
| 0 | 0 | 4 | -38 | slightly turbid |
| 0.06 | 0 | 6 | -32 | no change |
| 0.6 | 0 | 5 | -15 | turbid (very small flocs) |
| 1.3 | 0 | 10 | -7 | turbid (small flocs) |
| 1.9 | 0 | 11 | +10 | turbid (small flocs) |
| 6.0 | 0 | 12 | +33 | turbid (very small flocs) |
| 18 | 0 | 23 | +33 | slightly turbid (few flocs) |
| 30 | 0 | 34 | (+30) | slightly turbid (no flocs) |
| 1.9 | 1.0 | 14 | -22 | turbid (very large flocs of low density) |

^a Dow LS-1132-B, 910 Å diameter.

An alternative interpretation is that C-3 and A-22 in solution may form a complex which effects improved flocculation. The ζ measurements on mixtures of the two flocculants in the absence of the latex colloid indicate that the oppositely charged polyelectrolytes interact, although such particles are difficult to observe. Infrared examination of a similar mixture of the two flocculants also suggests such interaction. However, if on sequential addition there is interaction in solution, the end effect may be quite similar to that resulting from the interaction of the A-22 with the C-3 adsorbed on the colloid surface.

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