COAGULATION OF ILLITE AND OTHER CLAYS WITH ALUMINUM SULFATE

A Thesis

Presented in Partial Fulfillment of the Requirements
for the Degree of Master of Science

by

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INTRODUCTION

Purpose and Scope

Clays are one of the major causes of turbidity in natural waters. They are abundantly distributed over the earth's surface and readily gathered by water during surface flow in the hydrologic cycle. The removal of clay and other forms of turbidity from potable waters has been one of the problems with which the sanitary engineer has had to contend. In treatment plants the clarification of turbid waters is accomplished after the addition of small amounts of aluminum or ferric salts. For several years it was thought that the simple triply charged Al^{3+} and Fe^{3+} ions were the effective components of the salts which operated in the coagulation process. This notion was reinforced by Miller (26)(27) who after a number of investigations stated that the trivalence of aluminum and ferric ions was the predominant factor in coagulation. A few years later Mattson (20) controverted this view by concluding that the hydrolysis products of these metals were more effective than the three-plus ions in causing coagulation. Mattson's view was slow in gaining acceptance. Once accepted, however, new areas of research were opened for a number of new questions to be answered. For instance, what is the nature of these hydrolysis products? How are they affected by pH and concentration? What are their stoichiometrics, structures, and charges? What are their relative coagulating effectiveness at various pH values? What differences or similarities exist between the results obtained with one colloidal system and that obtained with another? If these questions are answered then the sanitary engineer will be able to apply an analytical rather than an empirical approach in determining the most economical coagulant dosage to be applied to a turbid water whose composition is known.

A great deal of research has been done with a view to answering some of these questions. In most of these investigations, however, natural waters of unknown or variable composition were used (3)(6)(9). The results of such investigations can be of limited use because whatever the results, these can only be applied to the specific water examined. Results that are of more fundamental value can be obtained if pure systems are used in the studies, for when the response of each to coagulation is known the response of natural despersions may possibly be projected. Tezak and Matijevic and co-workers have pioneered this line of research using silver halide sols. In collaboration with others (21)(22)(23) they have obtained the log concentration-pH domains of stability for the coagulation of several silver halide sols using aluminum nitrate and aluminum sulfate. Rubin and Hanna (35) and Hanna (15) have done similar work with the bacterium Escherichia coli. Some coagulation studies have been run with clays but as far as completing the stability domain is concerned such tests have been very scanty (30)(31).

With the coagulation studies that have been conducted procedures have varied from more or less standard "jar test" techniques to "nonmixing" methods. The present study is intended to determine the correlations existing between the two techniques and at the same time to investigate in a systematic study the coagulation of clays with aluminum sulfate. Specifically, this study is directed towards achieving the following objectives:

1. To compare the effects of high, low and zero alum concentrations on illite, kaolin and montmorillonite at various pH using a non-mixing procedure.

2. To correlate the results of non-mixing and jar test techniques for studying coagulation.

3. To establish the aluminum sulfate concentration-pH stability domain for the coagulation of illite.

The results obtained and the conclusions reached are limited by the following considerations:

1. The clays used are believed not to be absolutely pure.
2. Aluminum sulfate was the only hydrolyzing coagulant examined.
3. The tests were conducted at room temperatures which varied from 22°C to 28°C.
4. Illite and montmorillonite suspensions were aged for at least 10 days but not necessarily for a fixed length of time before use.
5. Although carbonate-free water was used only limited precautions were taken to prevent carbon dioxide from entering the test samples.

Early History of Coagulation

Turbidity removal is one of the oldest operations in water purification. For many centuries filteration was the best known method of performing this operation. Unfortunately, filteration has had some shortcomings. A significant amount of the particles causing turbidity are small enough to pass through the pores of the filters. A more efficient method was brought about when it became known that the addition of a small amount of alum (aluminum sulfate) would first increase the particle size by clumping ("coagulation"). The earliest description of the effect of alum on turbid water was made by Pliney in 77 A.D. (10) who reported that a mixture of alum and lime was found to be useful in rendering bitter water potable. Following this discovery, a number of individuals started applying alum to their drinking water. The introduction of alum into public water supplies was delayed for many more years because of fears of possible health hazards. It was not until 1881 that alum was first introduced into municipal water supplies at Bolton, England (33).

The earliest known research on coagulation was performed by D'Arcet (11) who in 1838 made a study of the coagulation of the Nile water with alum. His study was followed by Jeunet's in 1965 (10). Meanwhile other substances with coagulating power were being discovered. Among these were chlorinated copperas, ferric salts and other aluminum salts. In 1885 Austin and Wilber (1) conducted a comparative study of the known coagulants and concluded that aluminum sulfate was the most effective of them all. Their views were confirmed thirteen years later by Fuller (13). Fuller also stated that next to the aluminum salts, the ferric salts were the most powerful coagulants. Since then aluminum sulfate has been widely and predominantly used in water treatment practice. Its use, however, was based simply on rule of thumb as there was an inadequate knowledge of the chemistry of the reactions involved.

A greater understanding of the reactions of aluminum salts improved following the development of the hydrogen electrode in 1913. That year Blum (7) used the new instrument to refute the prevalent argument that aluminum salts cannot be redissolved under alkaline conditions. There were also other investigations which were centered on the effect of alkalinity on coagulation (3)(14)(27). It was a popular belief that the effectiveness of aluminum salts on coagulants was controlled by alkalinity. After 1920 a number of investigators (2)(3)(8)(17) realized that pH rather than alkalinity of the solution was the controlling factor both in the filtration and precipitation of alum floc. It then followed that if one were able to determine the proper pH for the coagulation and filtration of a particular water, one would have a simple method for controlling alum treatment. These workers were also able to show that the solubility of aluminum sulfate was minimum at neutral and near neutral pH values. Although emphasis has, so far, been laid on the experiments conducted with aluminum salts, most of the investigations reported were also performed on ferric salts with similar results. Further details are described in a history of coagulation by Packham (33).

Nature of Turbidity and Theory of Colloids

Turbidity is caused by very fine or colloidal particles suspended in a liquid medium. The colloidal matter prevalent in natural waters are clays and organic matter. These are collected as the water flows overland to the streams. The particles that constitute turbidity are so small that their surface area to mass ratios are extremely large. Under such conditions gravitational forces are negligible compared to the other forces acting on the particle. These forces can be classified under two headings: stabilizing and destabilizing forces. The destabilizing forces are those that tend to aggregate the particles and result from Van der Waal's forces of attraction and Brownian movement. The Brownian forces act to drive the particles momentarily close to one another. At the time of close proximity the Van der Waal's forces are tremendously increased. Stabilizing forces are a consequence of hydration and the surface charge of the colloidal particles. Hydration is the process by which water molecules are attracted to the surface of particles. The water molecules on the bound layer then act as a barrier to contact between particles.

Zeta potential is a measure of the "surface charge of colloidal particles which causes the particles to migrate in electric field to the pole of opposite charge" (5). The presence of an electrical charge on a colloidal dispersion was discovered by Reus in 1809 (41). In 1879 Helmholtz published a theory on the electrical phenomena at particle interfaces (10). He postulated two layers of opposite charges closely bound to the colloidal particle. The inner layer of charge resulted either from selective adsorption of ions or from residual valence forces. The inner layer charge, he believed, was balanced by an equal and opposite charge contributed by counterions. Nernst gave a practical demonstration in support of the Helmholtz theory when he showed, in 1889, that a metal immersed in solution of its ions will ionize and build up a double layer of charge at the solid-liquid interface (41). The fixed double layer concept was modified by Gouy and Chapman in 1910 and 1913, respectively. They pointed out that because of thermal and other diffusive forces it was impossible to maintain a fixed outer layer of counterions. The resultant effect of surface charge attraction and diffusion of the counterions would be the creation of a diffuse layer of ions. At a great distance from the particle the concentrations of ions of opposite charges would be equal, but as the particle interface is approached the concentrations of ions with charge opposite to surface charge increase while the concentration of ions of similar charge decrease.

The modern concept of the electrical double layer was developed by Stern in 1924 (41). According to this concept, because of their size the closest counterions are centered at some distance from the surface of the particles. Between this center and the surface, known as the Stern layer, the electric potential decreases linearly with distance. Beyond the center the diffuse layer of Gouy and Chapman apply. Some distance into the diffuse layer a plane of shear exists and all ions enclosed by the plane are dragged along as the particle executes random motions in the dispersion medium. The resultant charge at the plane of shear is known as the zeta potential. It is this charge that is responsible for the migratory tendency of the colloid in the electric field.

Colloids may be classified as either lyophilic or lyophobic. Lyophilic colloids are those which have an affinity for the dispersion medium. In other words, the medium itself contributes to their stability. They are easily dispersed and can be redispersed after drying. The lyophobic colloids usually are difficult to disperse; if dried, redispersion is almost impossible. Packham (32) has listed the properties of lyophobic and lyophilic colloids and has remarked that "the distinction between the two classes of colloids is not fundamental" and that "a continuous series of substances exist with properties intermediate between the two extremes."

Clay Structures

Clay minerals are hydrous aluminum silicate compounds consisting of alternating layers of tetrahedral silica and octahedral hydrous aluminum oxide. The negative surface charge on clays is a consequence of isomorphous substitution of tetravalent silicon and trivalent aluminum atoms by divalent atoms such as magnesium, iron, chromium, zinc, and lithium (25).

The unit cell of the kaolinites is two-layered. A layer of silica is covalently bonded to a layer of hydrous aluminum oxide. The extent of metal atom substitution is small, giving rise to low surface charge and low cation exchange capacity. Particles of kaolin usually consist of several unit cells held together by hydrogen bonds. Illite and montmorillonite clays have unit cells with a layer of hydrous aluminum oxide sandwiched between two layers of silica. Compared to kaolin these two clays possess greater surface charge because of greater isomorphous substitution of metal atoms in the cell lattice. The unit cells of illite are bonded into larger particles by metal ions, mostly potassium ions, while the unit cells of montmorillonite are united by water molecules whose positive dipoles have been oriented towards the negative surfaces.

The varying ease ~~with~~ which each of the clays can be dispersed is explained by the type of bond between unit cells. Kaolin is the hardest to disperse because the strength of the covalent bond formed by hydrogen opposes the break up of its particles. In illite the potassium bond is ionic. As ionic bonds are more easily disrupted in water than covalent bonds, illite particles break up and disperse to a greater extent. The bonds provided by water molecules are the weakest and explain why montmorillonite readily disperses (25)(41).

Mechanisms of Coagulation

One of the ways by which electrolytes destabilize colloids is through the reduction of the electrical forces of repulsion between particles. When salts are added to a colloidal system the ionic content of the system is increased. As a result of chemical or electrostatic attraction the counterions (coagulating ions) from the salt are preferentially attracted to the colloid surface. Consequently, the ratio of counterions to nebenions (ions of charge opposite to the counterion) increases upon approaching the surface of the colloid. This increase leads to the reduction of the protective electric potential around the colloid. Sufficient reduction in electric potential allows the particles, under Brownian motion, to approach each other to the point where the Van der Waal's forces of attraction exceeds the electrical repulsion between the particles. At this juncture coalescence follows and particle growth leads to settling. The above mechanism is regarded as true coagulation or simply coagulation. It represents the destabilizing action of simple electrolytes on lyophobic sols. Schulze and Hardy showed that when true coagulation occurs the effect of the counterion is related to the sign of its charge and that the coagulating power is an exponential function of the magnitude of the charge (16). A theoretical formulation of the coagulating power of counterions was also presented by Verwey and Overbeek (42), and Tezak and collaborators (40).

In water treatment processes aluminum and iron salts are most generally used. These, being hydrolyzing salts, are considerably influenced by the pH of the solution. The mechanism by which they cause clarification is complicated and not yet well understood. Matijevic and co-workers have presented considerable evidence that these salts act according to the Schulze-Hardy rule. A number of ionic species of aluminum have been suggested as being mainly responsible for coagulation. Some of these that have been suggested are $Al_8(OH)_{20}^{4+}$, $Al_7(OH)_{17}^{4+}$ and $Al_{13}(OH)_{35}^{4+}$ (4). Other investigators, however, have presented other views. Langlier and Ludwig (19); Rubin, et al. (36); Tenney and Stumm (39) have stated that the hydrolysis products of aluminum causes agglomeration by the formation of bridges between particles. This last mechanism is distinguished from true coagulation and is termed flocculation. Packham (29), after coagulating clay with aluminum sulfate, did not believe that his results could be explained in terms of the flocculation or "binder alum" theories, rather he was convinced that between pH 5.5 and 7.5 where aluminum sulfate was most efficient as a coagulant, agglomeration was principally due to the enmeshment of the "precipitating and flocculating aluminum hydroxide." Rubin and Lackey concur (37). Another mechanism which has also been reported is mutual coagulation. In mutual coagulation oppositely charged colloids act as "counterions" to one another. McAtee and Wells (24) have produced electron micrographs of clays coagulated with an aluminum salt to show that mutual adsorption occurs between negatively charged clay particles and positively charged aluminum oxide. Theoretical treatments of the mechanism of mutual coagulation are given by Hogg, et al. (18) and Weiser and Chapman (43).

Obviously there is no general agreement on the mechanism of coagulation by hydrolyzing salts. Views are diverse but may not be actually contradictory. Some of the mechanisms may be peculiar to the systems under investigation. For instance, most of the authors who have reported the bridging mechanism worked with materials which possess chemically active groups on their surfaces. The opposing views of Matijevic and Packham can also be explained if it is realized that Packham interpretated the mechanism that obtained at high concentration of coagulant where precipitation of alum floc was extensive while Matijevic interpretated his results obtained in the absence of excess aluminum. It is not unlikely therefore that for the same coagulant different mechanisms may predominate at different concentration or pH. It is also evident that the role of precipitation in the chemical "coagulation" process needs to be given further consideration.

Chapter II

EXPERIMENTAL METHODS AND MATERIALS

Solutions and Suspensions

Three clays obtained from Wards Natural Science Establishment were tested. These were illite #48W1535 from Fithian, Illinois; kaolin #37W1330 from an unspecified source; and montmorillonite (bentonite) #20 from Husband Mine, Polkville, Mississippi. Identical procedures were used to prepare and disperse the clays. The lumps of clay were first crushed in a porcelain mortar and then transfered to a ball mill where further grinding was continued for three days. After grinding, batches of about 2 grams were mixed with 600 ml of deionized double distilled water. This mixture was vigorously stirred at a high speed for 15 minutes with a Waring blender in order to hydrate the clays and to disperse them in the liquid. Approximately five batches of the blended clay suspensions were diluted in a 15-liter carboy to obtain a transmittance reading of 10 to 15% at 400 mu in a 19 mm cell. The clay was mixed and kept in suspension by stirring with a magnetic stirrer. After 10 days suspensions of illite and montmorillonite were settled for 12 hours and finally siphoned into another 15-liter carboy in which the suspension was also stirred continuously. Kaolin suspensions were settled for about 10 hours without the 10-day mixing and storage because it was found that storage made the suspensions much more unstable. The solid contents of the suspensions were determined by evaporating a sample with known absorbance reading and then weighing the residue. It was found that clay concentration was directly proportional to absorbance reading. Therefore the solid content of any other sample was determined from direct proportionality. The final clay concentrations of tested samples were 160 mg/l for kaolin and illite, and 330 mg/l for montmorillonite.

Aluminum sulfate (alum) stock solutions were freshly prepared each day of testing from reagent grade $Al_2(SO_4)_3 \cdot 18H_2O$. A minimum of 1 gm of chemical was accurately weighed and dissolved in a liter of deionized double distilled water which was prepared by passing steam condensate through a deionizer and then redistilling. Whenever further dilution was necessary at least 100 ml of the stock solution was used. These solutions were kept in polyethylene bottles. All concentrations are reported as moles per liter aluminum(III). Solutions of sodium nitrate and calcium nitrate were prepared from the reagent grade salts in the same manner as described for aluminum sulfate. These salts, however, were not prepared daily.

Approximately 1 N solution of reagent grade nitric acid was prepared and standardized against tris(hydroxymethyl)aminomethane (12). The nitric acid solution was used as a secondary standard to standardize 1 N sodium hydroxide prepared from the reagent grade pellets. These were prepared with deionized double distilled water and were used for pH adjustment. They were also stored in polyethylene bottles.

Equipment and Procedure

Some of the tests were run using a Phipps and Bird 6-place multiple stirrer ("jar test apparatus"). The apparatus was modified in a manner similar to that described by Cohen (9). The main feature of the modification was the addition of an aspirator connected with a manifold having six needle valves. Connections were made with rubber tubing to the sample containers and from these to the reaction vessels. This arrangement allowed simultaneous sampling of the six reaction vessels.

In order to keep the clay suspension concentrations constant the stock suspension was always diluted before use, so that the absorbance measurement with a Coleman Model 14 spectrophotometer would read 0.566 at 400 mu. This wavelength was chosen for maximum sensitivity. Just before experimentation six 800-ml beakers containing 425 ml of clay suspension were placed under each stirrer. Six 100-ml beakers containing 25 ml aluminum sulfate were also prepared. For pH adjustment, acid (when needed) was always added to the alum solutions and base (when needed) was always added to the clay suspensions. Thus premature precipitation of aluminum hydroxide or acid coagulation of the clay was avoided. The total volume of acid or base added with distilled water was always kept constant at 50 ml. Fast mixing was started immediately after preparing these solutions. The alum solution was then added to each of the beakers in as short a period of time as possible and a stop watch was started. Fast mixing at 90 rpm was continued for 10 minutes after which slow mixing at 5 rpm was begun. Samples were siphoned directly into Coleman 19-mm round cuvettes for measurement at the end of 5 minutes and 20 minutes of slow mixing. The turbidity was estimated by absorbance measurements using a Coleman Model 14 spectrophotometer at 400 mu. The pH corresponding to each absorbance reading was measured using a Sargent Model DR pH meter and Sargent combination electrode.

The jar test apparatus was also used to determine the critical coagulation concentration of alum. The critical coagulation concentration, or c.c.c., is the amount of coagulant just needed to cause destabilization and settling. The procedure was the same as just described but with the following two differences. Firstly, no pH adjustment was necessary since it was found that at very low concentration of alum the pH did not vary significantly. Secondly, the final content of each 800-ml beaker differed from the other in alum concentrations rather than in pH.

In addition to "jar tests" other tests were run employing the "non-mixing" technique described by Rubin and Hanna (35). In this second series of tests clay suspension was kept with base in small glass vials while alum solution was kept with acid in the cuvettes. A total of 15 ml of sample consisting of 10 ml of clay suspension, 3 ml of alum and 2 ml of acid or base was shaken vigorously in Coleman 19-mm round cuvettes for 15 seconds and then set aside without any further mixing. Absorbance readings were made on the samples after 15 minutes, 1, 3, 6 and 12 hours from the time of mixing. Usually a series of 10 to 15 cuvettes were run. Preliminary investigations indicated that the pH of the samples changed only very little with time. Therefore the pH of the entire test series was measured only once and within the first hour. Thereafter pH was measured at the same time as the absorbance measurements were made and only on samples in pH ranges where the absorbance-pH curve was expected to drop or rise rapidly.

"Non-mixing" procedures were also used to determine the c.c.c. of alum and the neutral salts. For these tests the total 15 ml of sample consisted of 10 ml of clay and 5 ml of alum or neutral salt of varying concentrations. As before no pH adjustment was deemed necessary. For all non-mixing tests the clay was diluted to obtain an absorbance reading of 0.806 at 400 mu. With this reading the initial absorbance reading of the final mixture would be 0.538. Calculation of initial absorbances of the mixtures were based on the finding that absorbance is directly proportional to clay concentration. The same value of initial turbidity would be expected for the jar test samples.

Jar tests and non-mixing tests were run on the clay suspensions without the addition of alum so as to determine the effect of pH on the clays. For all tests described, a blank suspension consisting of clay and water was always included in the runs for control purposes.

Treatment of Data

For each concentration of aluminum the absorbance of the samples was plotted against the pH. Typically these plots had alternating pH ranges of coagulation and stabilization. The steep portions of the curves were extrapolated to obtain the critical pH for coagulation and stabilization. These were designated pH_c and pH_s, respectively. The pH_s is defined as the limiting pH above which restabilization or stabilization occurs while pH_c is defined as the limiting pH below which restabilization or stabilization occurs. Therefore coagulation occurs in the pH range between the pH_c and the pH_s and restabilization occurs in the pH range between the Ph_s and the pH_c. Generally, the pH_s values were obtained from the extention of positive slopes and pH_c values from the extention of negative slopes. Two methods of extrapolation were considered. The first method involved extrapolating to the initial absorbance of the blank and the second involved extrapolating to zero absorbance. The plot of pH_s and pH_c as abscissa and logarithm of corresponding aluminum concentration as ordinate was used to establish the domain of stability for the suspensions. The choice of method of extrapolation was based on the correlation obtained from preliminary plots of the domain of stability. For the c.c.c. tests the turbidity of the samples were plotted against aluminum concentrations. The slopes of the curves were extrapolated in the same manner as the pH turbidity curve to obtain the critical coagulation concentration. The pH of the sample whose plot was nearest to the extrapolated point was recorded as the critical coagulation pH.

Chapter III

EXPERIMENTAL RESULTS

Non-mixing Studies

The effect of pH without the addition of alum on the stability of illite, kaolin and montmorillonite was examined using the "non-mixing" technique for studying coagulation. These studies showed that the clays are coagulated by hydrogen ion. The addition of acid to suspensions of montmorillonite produced immediate coagulation below pH 2.8. Within 15 minutes of mixing the turbidities of the coagulated samples were less than 30 per cent of their initial value. Further coagulation occurred at higher pH with the passage of time so that at the end of 12 hours the limiting pH for coagulation rose from 2.8 to 3.4. Above pH 3.4 and up to pH 10.0, the highest pH examined, the montmorillonite suspensions were stable for over 24 hours.

The effects of pH on the stability of illite and kaolin were identical in many respects. Coagulation was first observed in samples having pH less than 4.6 in about 30 minutes. In the first hour the reduction in turbidity was less than 30 per cent for both clays. Rapid settling, however, started soon after 1 hour so that by the end of 3 hours the turbidity remaining was less than 20% of the initial. The limiting pH for coagulation also increased with time as was observed for montmorillonite. For both clays the increase was from pH 4.6 at 3 hours to pH 5.0 at 12 hours. Suspensions of the two clays were stable for over 24 hours in the pH range 5.0 to 10.0.

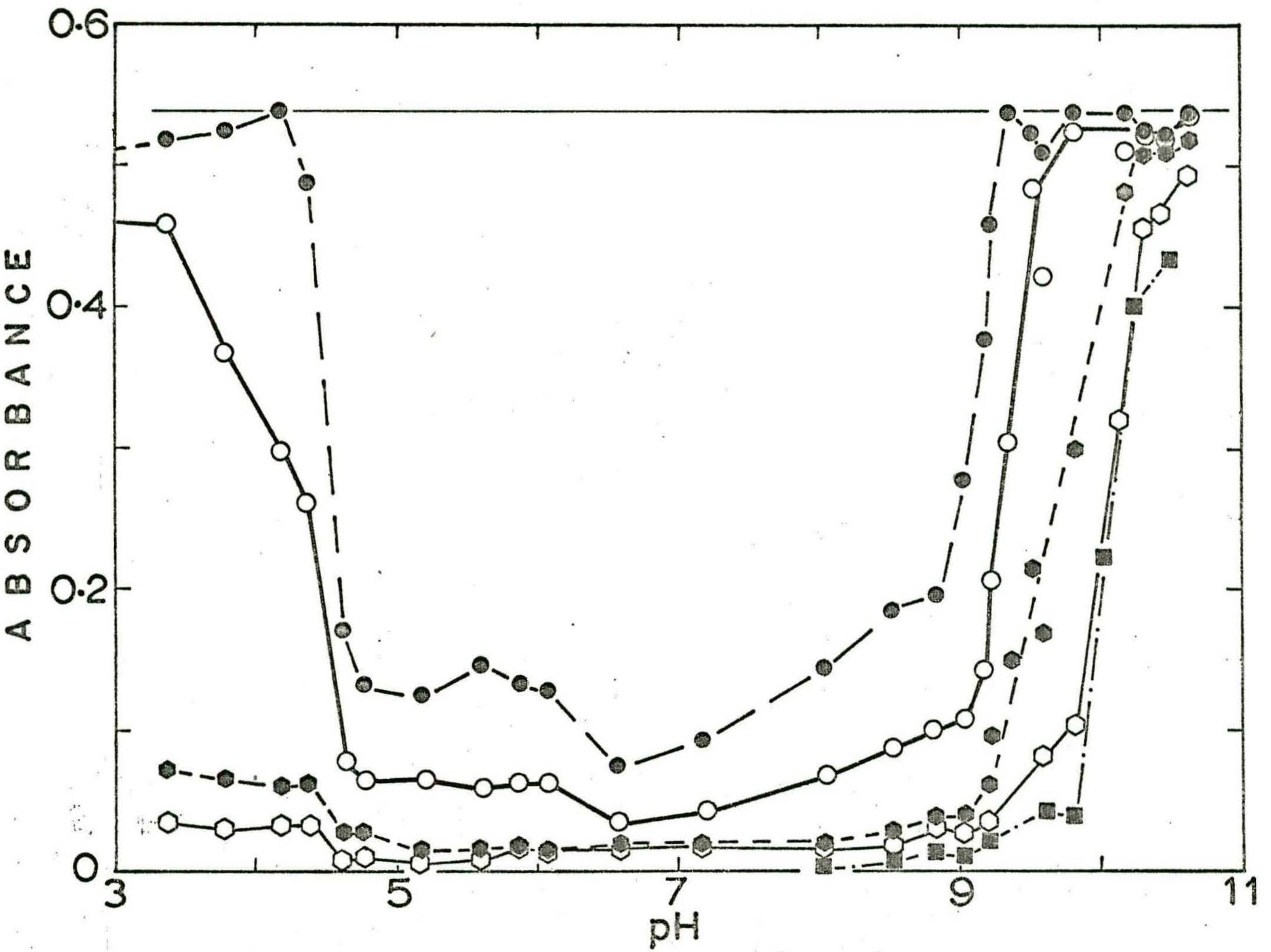

Figure 1. COAGULATION OF ILLITE BY 1.0 x 10^{-3} M $Al(SO_3)_{3/2}$. NON-MIXING TESTS.

Blackened circles are 15 minute, open circles are 1 hour, blackened hexagons are 3 hour, open hexagons are 6 hour, blackened squares are 12 hour measurements.

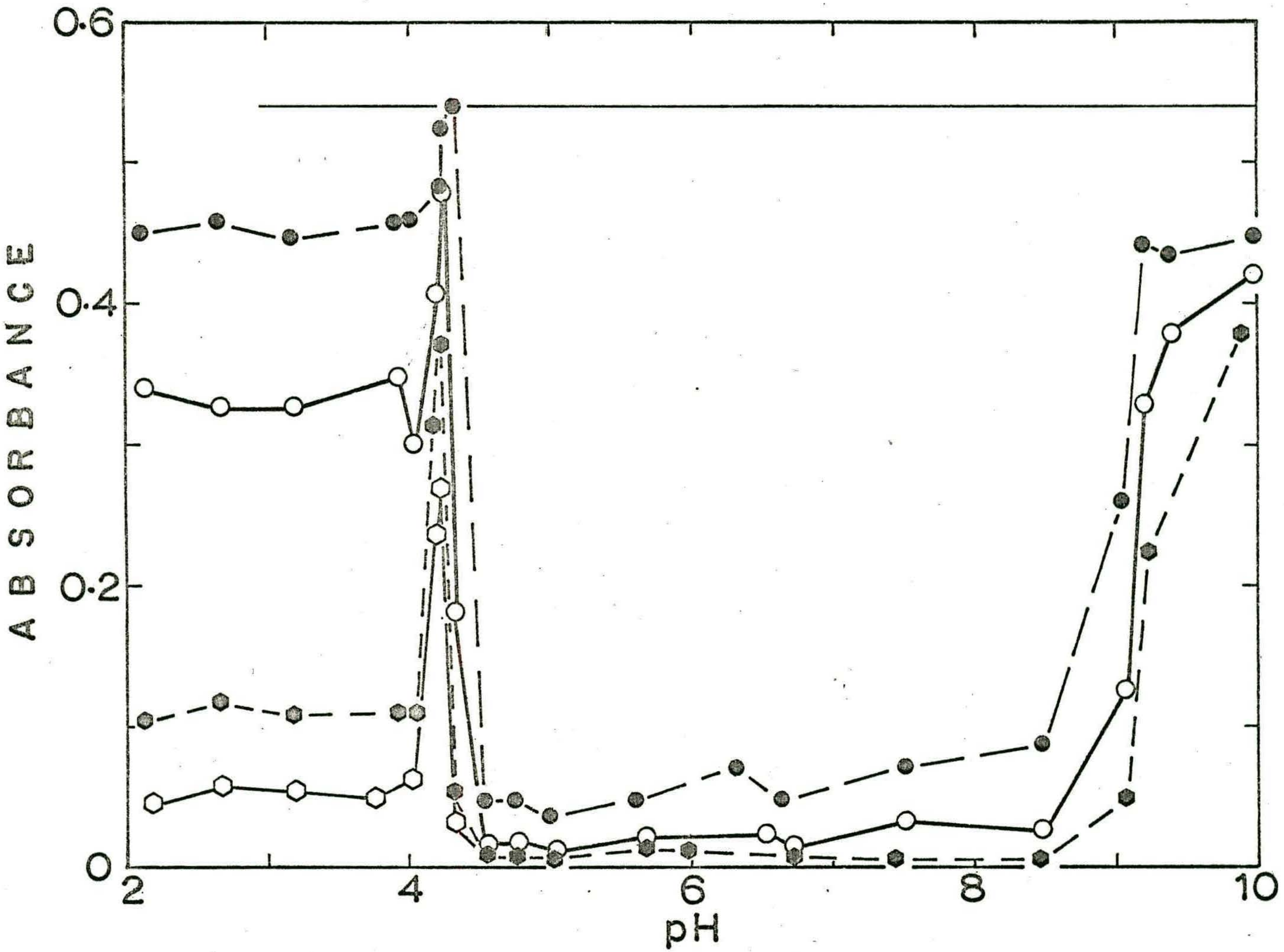

Figure 2. COAGULATION OF KAOLIN BY 1.0 x 10^{-3} M $Al(SO_4)_{3/2}$. NON-MIXING TESTS. Symbols explained in Figure 1.

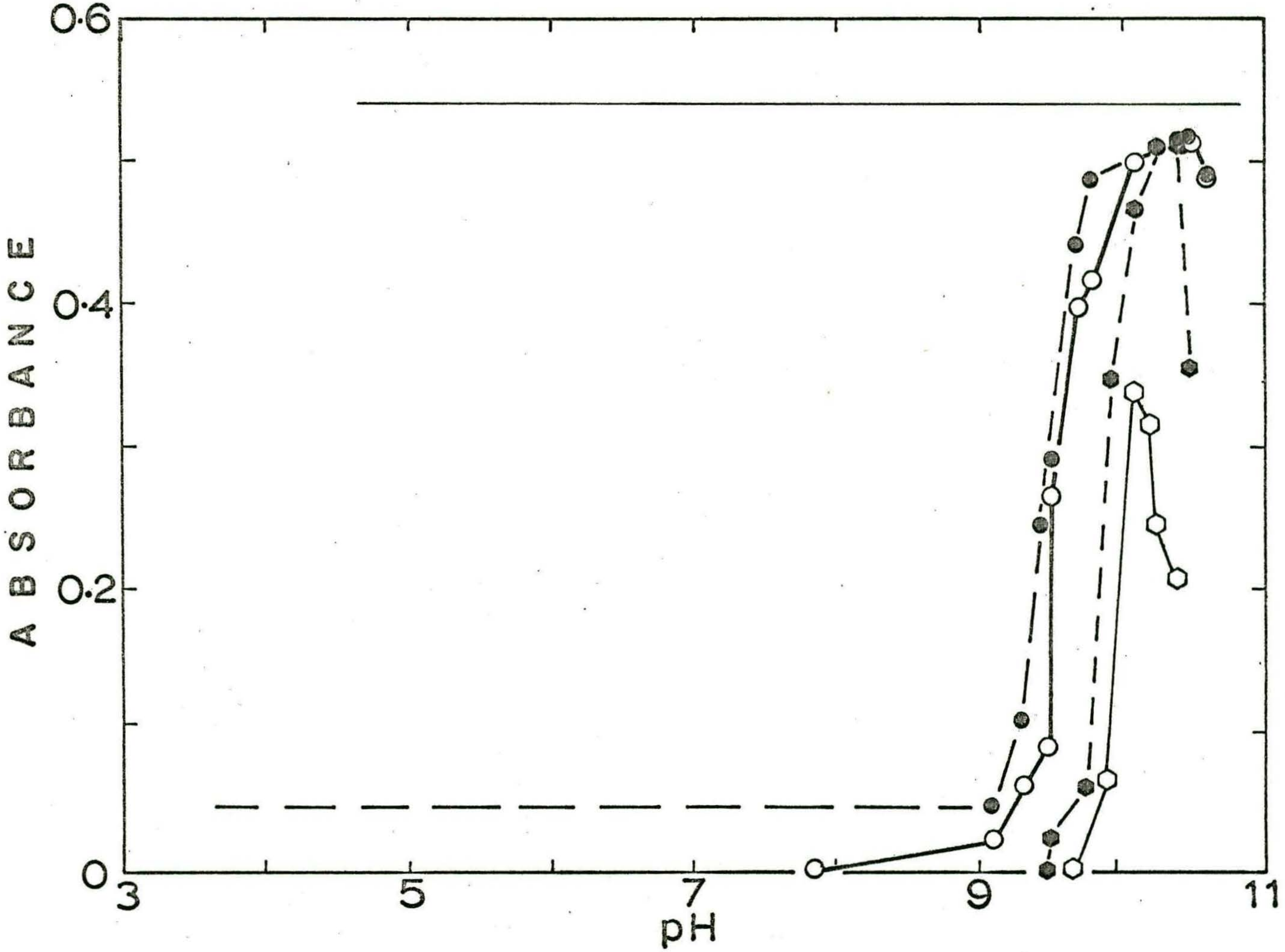

Figure 3. COAGULATION OF MONTMORILLONITE BY 1.0 x 10^{-3} M $Al(SO_4)_{3/2}$. NON-MIXING TESTS. Symbols explained in Figure 1.

The effect of aluminum sulfate on the three clays was investigated using Al(III) concentrations of 1×10^{-3} M and 1×10^{-4} M. Figure 1 shows the relationship between absorbance and pH for suspensions of illite treated with 1×10^{-3} M $Al(SO_4)_{3/2}$ using the non-mixing technique. The curve has three sections. The middle one, lying between pH 5 and pH 9, represents a range of rapid clarification (i.e., the "sweep zone"). To its left is a region of slow coagulation and to the right a region of stability (i.e., no coagulation). The figure also shows a time dependent shift to the right of the boundary between rapid clarification and stability. This shift may be a consequence of slow coagulation by sodium ions added with the base. As shown in Figure 2 very similar results were obtained when kaolin was treated with the same amount of alum; the pH ranges of the sweep zones for both clays are almost identical. The only significant difference is the presence of a narrow restabilization region between pH 4.0 and pH 4.5. The effect of 1×10^{-3} M $Al(SO_4)_{3/2}$ on montmorillonite is shown in Figure 3. A noticeable characteristic is the absence of a temporary stability zone at low pH resulting in the apparent rapid coagulation of the clay over a wider pH range. This was expected since montmorillonite coagulates fairly rapidly at low pH in the absence of aluminum sulfate. The clay was stable in the pH range 9.5 to pH 10.1 and apparently unstable at higher pH.

At a lower Al(III) concentration, 1.0×10^{-4} M $Al(SO_4)_{3/2}$ as shown in Figures 4 and 5 for illite and kaolin, respectively, the sweep zones were narrower and there were fairly broad central zones of restabilization. Vestiges of these stability regions were apparent after 24 hours with kaolin, but illite settled out within 3 hours. It is

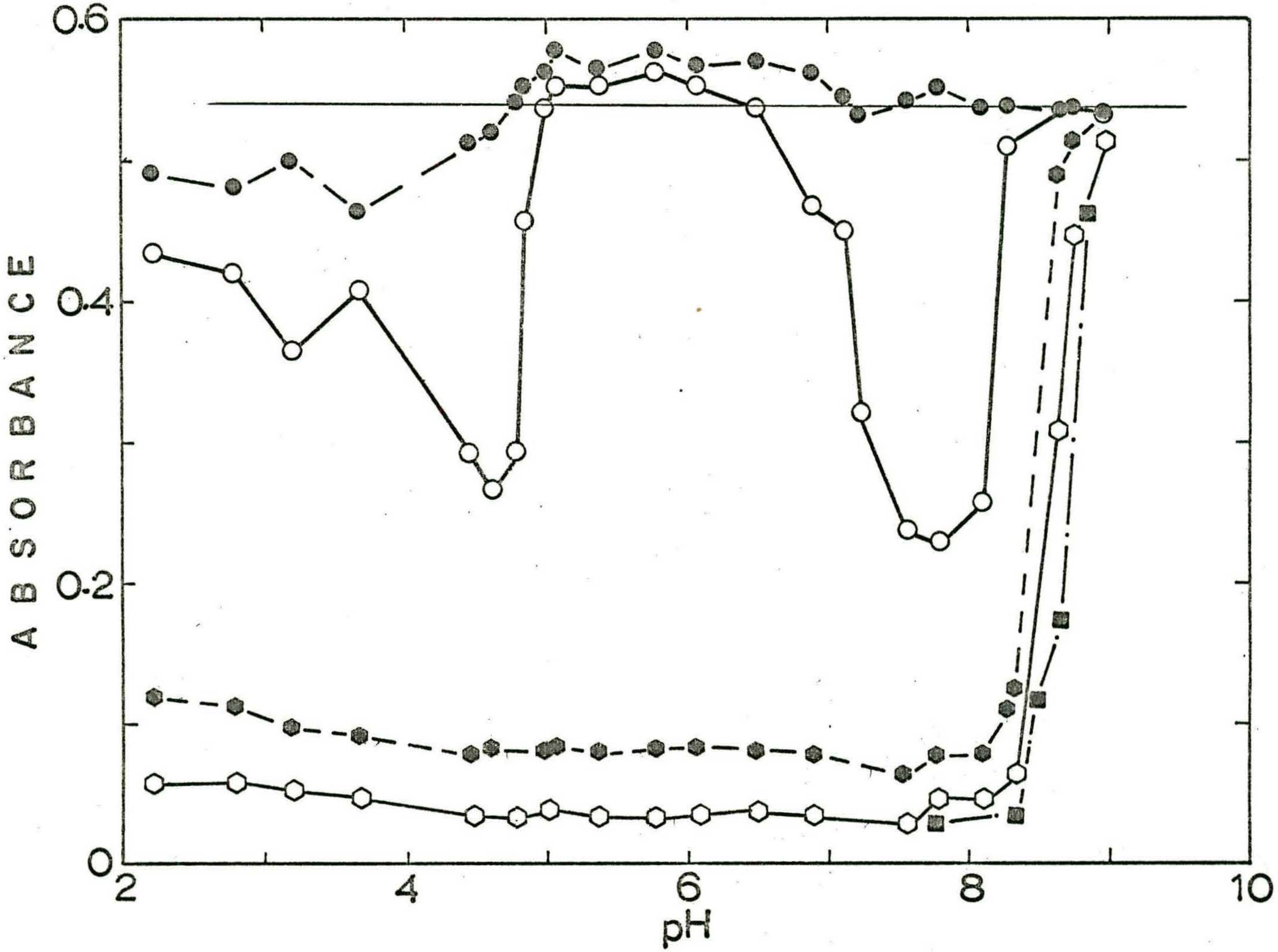

Figure 4. COAGULATION OF ILLITE BY 1.0 x 10^{-4} M $Al(SO_4)_{3/2}$. NON-MIXING TESTS.

Symbols explained in Figure 1.

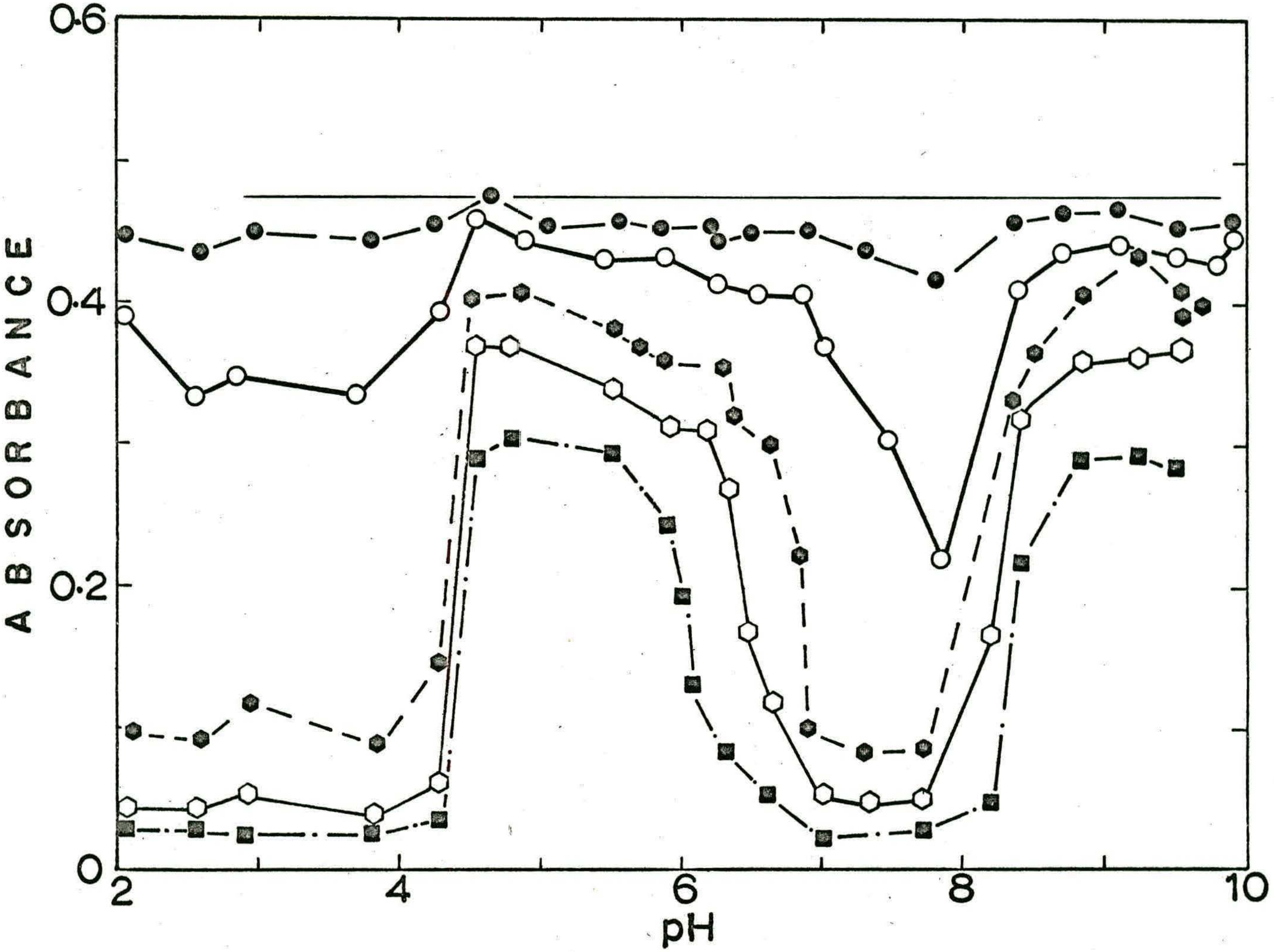

Figure 5. COAGULATION OF KAOLIN BY 1.0 x 10^{-4} M $Al(SO_4)_{3/2}$. NON-MIXING TESTS.

Symbols explained in Figure 1.

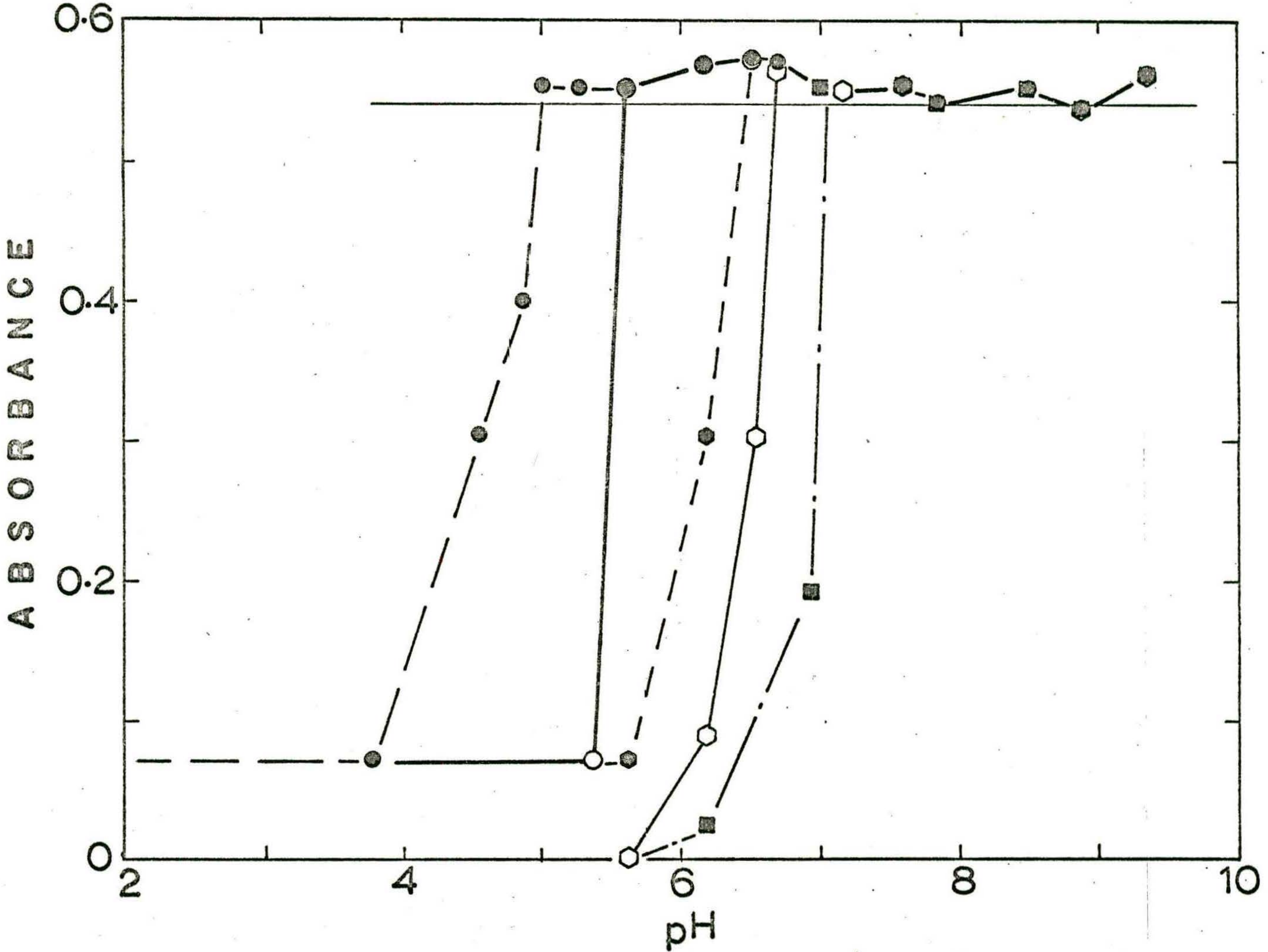

Figure 6. COAGULATION OF MONTMORILLONITE BY 1.0 x 10^{-4} $\underline{M}$ $Al(SO_4)_{3/2}$. NON-MIXING TESTS. Symbols explained in Figure 1.

suspected that this difference in behavior with the two clays resulted because the kaolin suspensions were not aged before coagulation. As mentioned earlier aging made the kaolin suspension more unstable. But even without aging, the kaolin suspensions were less stable than suspensions of either of the other two clays. Consequently, as shown in Figure 5, there was a significant drop in absorbance readings at all pH values. The effect of 1×10^{-4} $\underline{M}$ $Al(SO_4)_{3/2}$ on montmorillonite is shown in Figure 6. Again there was no region of stability at intermediate pH and settling occurred over a wide pH range. The effect of reducing the Al(III) concentration from 1×10^{-3} $\underline{M}$ to 1×10^{-4} $\underline{M}$ was to significantly reduce the limiting pH for stability. At the lower concentration this limiting pH is also shown to be more time dependent.

Critical coagulation concentrations (c.c.c.) were determined for illite by mixing varying concentrations of alum with suspensions of the clay. The mixing was done in 19 mm cuvettes and absorbance readings were taken at 15 minutes, 1, 3, 6 and 12 hours. Figure 7A shows that if 12-hour measurements are used and the steepest slope of the absorbance-log aluminum concentration curve is projected to zero absorbance the value of the c.c.c. is 3.1×10^{-5} $\underline{M}$ $Al(SO_4)_{3/2}$ at pH 6.7. Acid or base adjustment was not made with these tests because there was little variation in pH over the Al(III) concentration range examined. Results shown in Figure 7B demonstrate that the addition of NaOH had the effect of lowering the c.c.c.

As expected, pH variations in the illite suspensions upon adding neutral salts were insignificant. The pH for the illite mixtures under sodium and calcium nitrate was 7.35 ± .05. The critical coagulation concentrations were obtained by plotting a graph of absorbance against

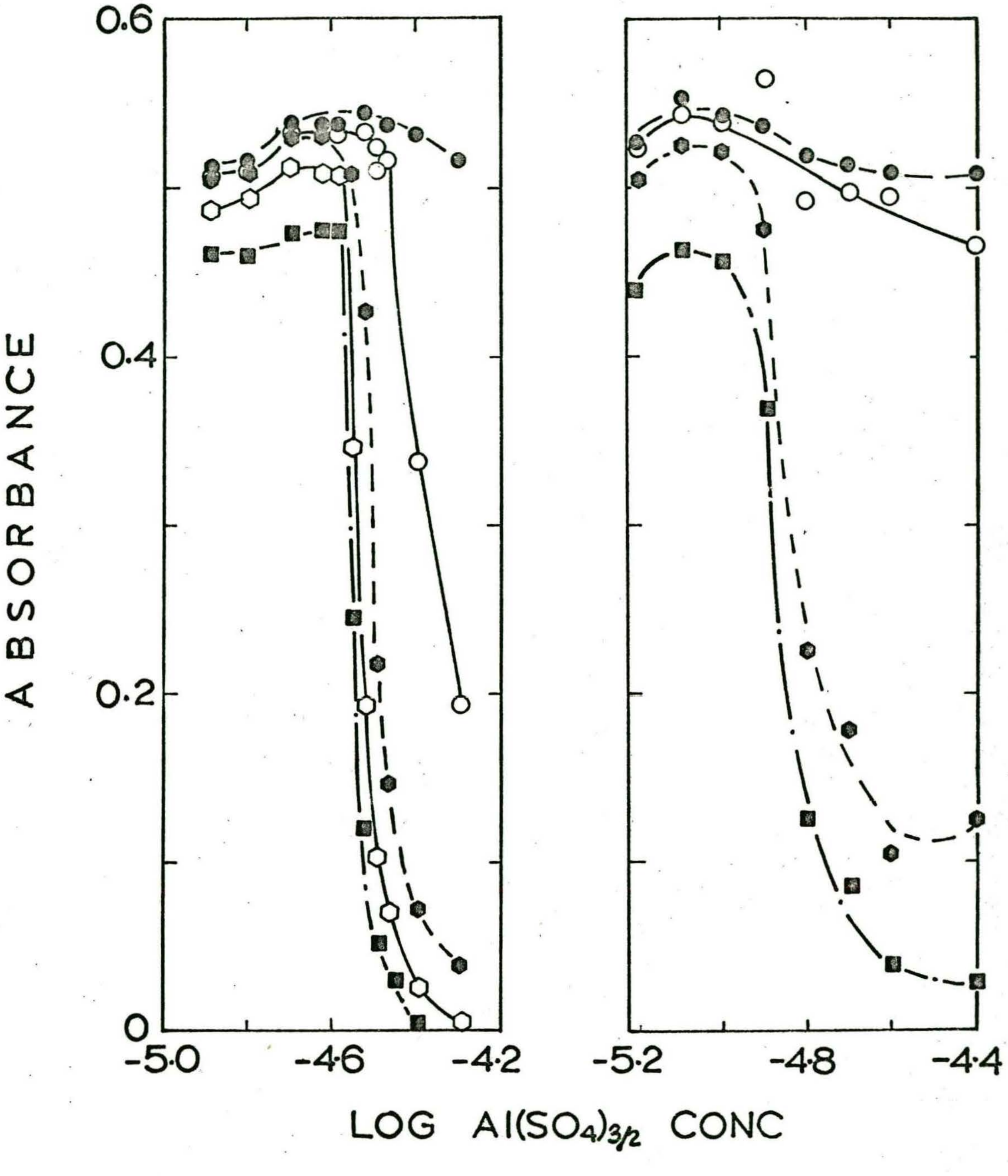

Figure 7. COAGULATION OF ILLITE AS A FUNCTION OF ALUMINUM SULFATE CONCENTRATION NEAR NEUTRAL pH RANGE. NON-MIXING TESTS.

Symbols explained in Figure 1.

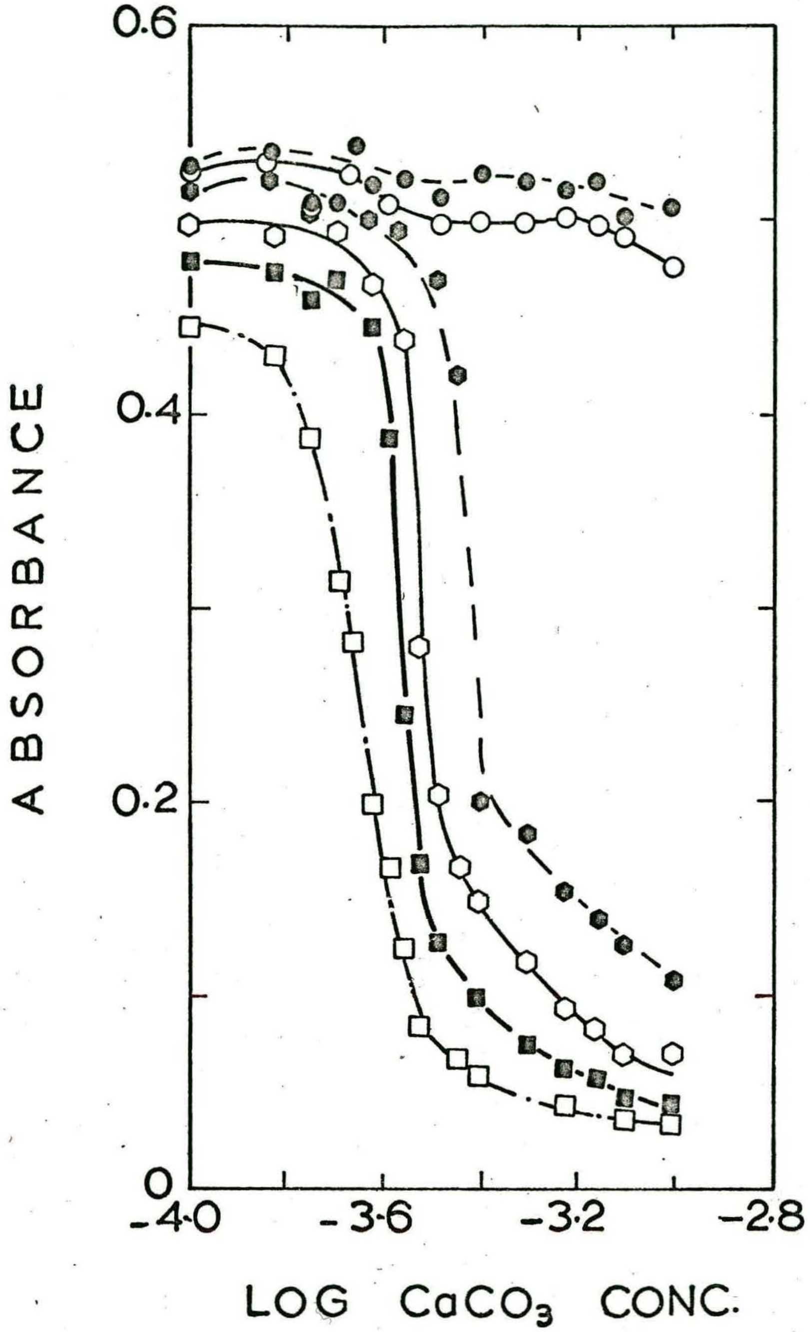

Figure 8. COAGULATION OF ILLITE AS A FUNCTION OF CALCIUM NITRATE CONCENTRATION. NON-MIXING TESTS.

Blackened circles are 15 minute, open circles are 1 hour, blackened hexagons are 3 hour, open hexagons are 6 hour, blackened squares are 12 hour measurements, open squares are 24 hour measurements.

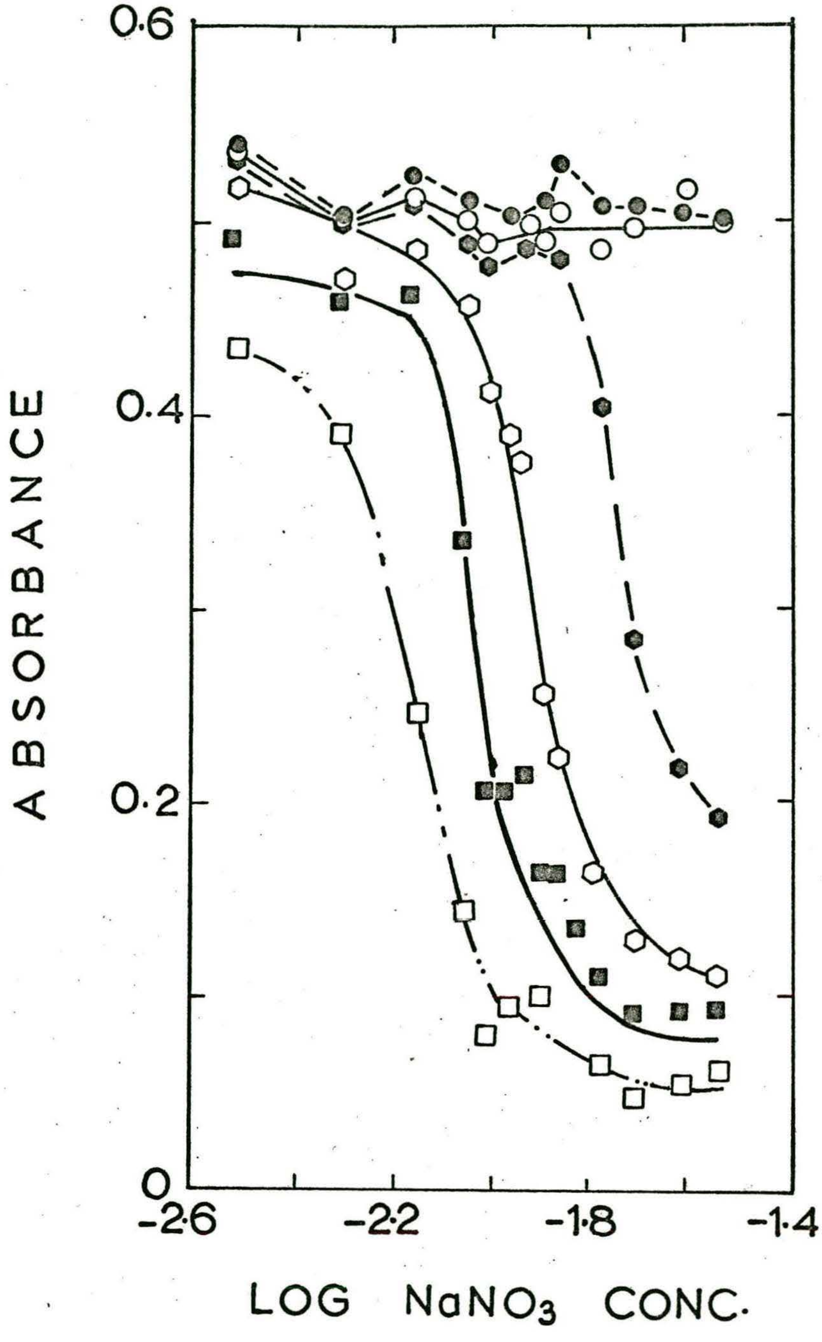

Figure 9. COAGULATION OF ILLITE AS A FUNCTION OF SODIUM NITRATE CONCENTRATION. NON-MIXING TESTS.

Blackened circles are 15 minute, open circles are 1 hour, blackened hexagons are 3 hour, open hexagons are 6 hour, blackened squares are 12 hour, open squares are 24 hour measurements.

the log molar concentrations of the salts and extending the steepest slope of the 12-hour data to zero turbidity. The 12 hour data were used for the extrapolations since changes in the values of the c.c.c. were insignificant after this time. These graphs are presented in Figures 8 and 9. A comparison of Figures 7, 8 and 9 reveals that not only is the c.c.c. of $NaNO_3$ less than that of $CaNO_3$, which is less than that of $Al(SO_4)_{3/2}$, but also the time dependency of the c.c.c. follows the same order. The critical coagulation concentrations of calcium nitrate and sodium nitrate were, respectively, 1.3 x 10^{-4} M and 1.5 x 10^{-2} M.

Jar Test Studies

Studies on the coagulation of illite over the $Al(SO_4)_{3/2}$ concentration range of 10^{-6} to 10^{-1} M were performed using the jar test apparatus. Typical results are shown in Figures 10 through 15. At most concentrations of aluminum typical pH ranges of slow coagulation, stabilization, and rapid clarification are evident. At high concentrations, as shown in Figure 10 for 1.6 x 10^{-3} M $Al(SO_4)_{3/2}$, the sweep zone was very wide and there was no central restabilization zone. Upon reducing the concentration to 3.16 x 10^{-4} M, as shown in Figure 11, restabilization occurred in the narrow pH range of 4.4 to 5.0. Further reduction in concentration to 2.4 x 10^{-4} M resulted in significant widening of the restabilization range. Figure 12 also shows this effect and demonstrates that the widening is a result of encroachment into the rapid clarification range. As can be seen from Figure 13 restabilization covered a very wide pH range at 1 x 10^{-4} M $Al(SO_4)_{3/2}$. The maximum absorbance in the restabilization region exceeded the initial absorbance of the

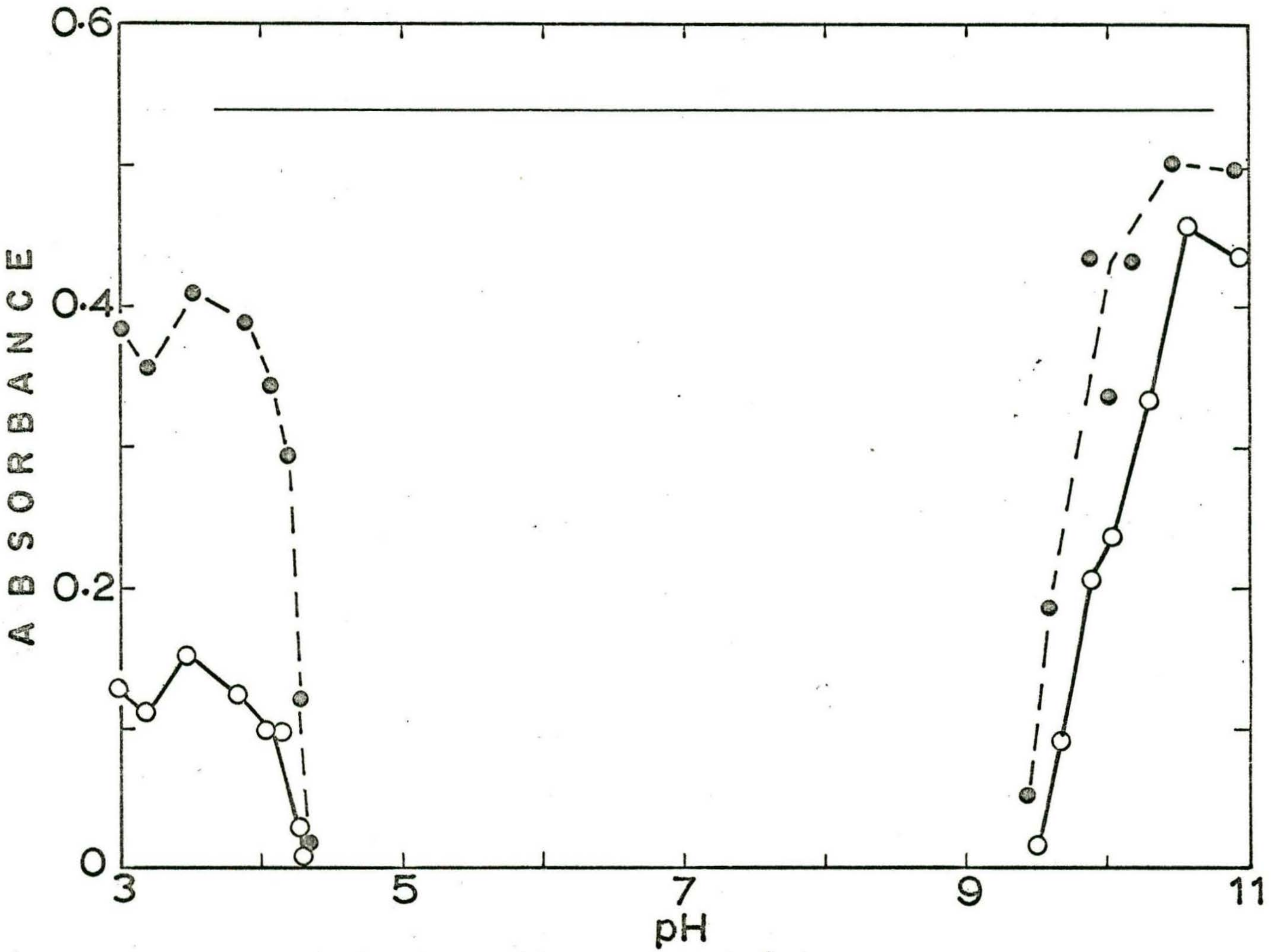

Figure 10. COAGULATION OF ILLITE BY 1 x 10^{-3} M $Al(SO_4)_{3/2}$. JAR TESTS.

Fast mix 10 minutes at 90 rpm. Blackened and open circles respectively show measurements taken after 5 and 20 minutes of slow mix.

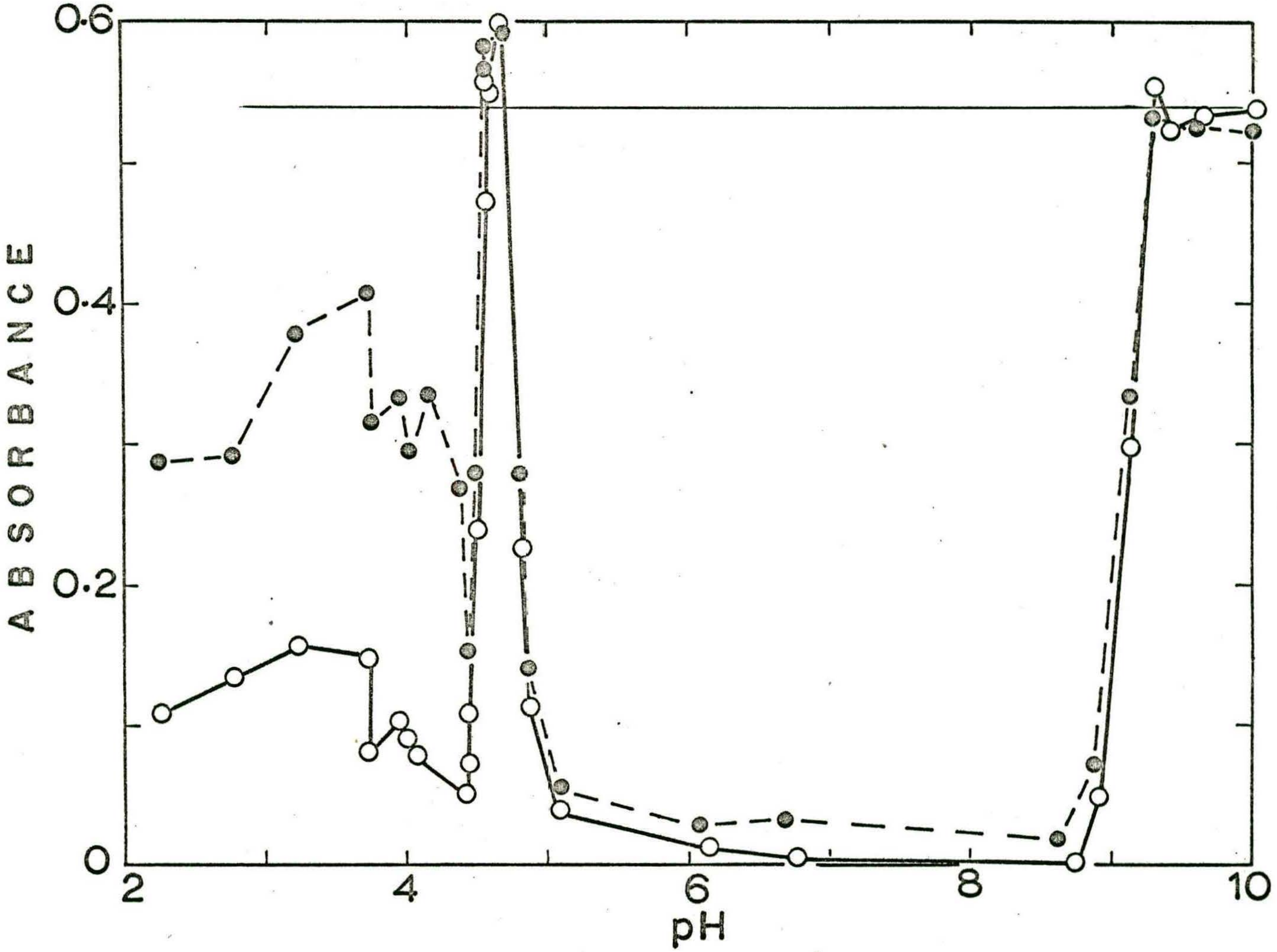

Figure 11. COAGULATION OF ILLITE BY 3.16 x 10^{-4} $\underline{M}$ $Al(SO_4)_{3/2}$. JAR TESTS.

Fast mix 10 minutes at 90 rpm. Blackened and open circles respectively show measurements taken after 5 and 20 minutes of slow mix.

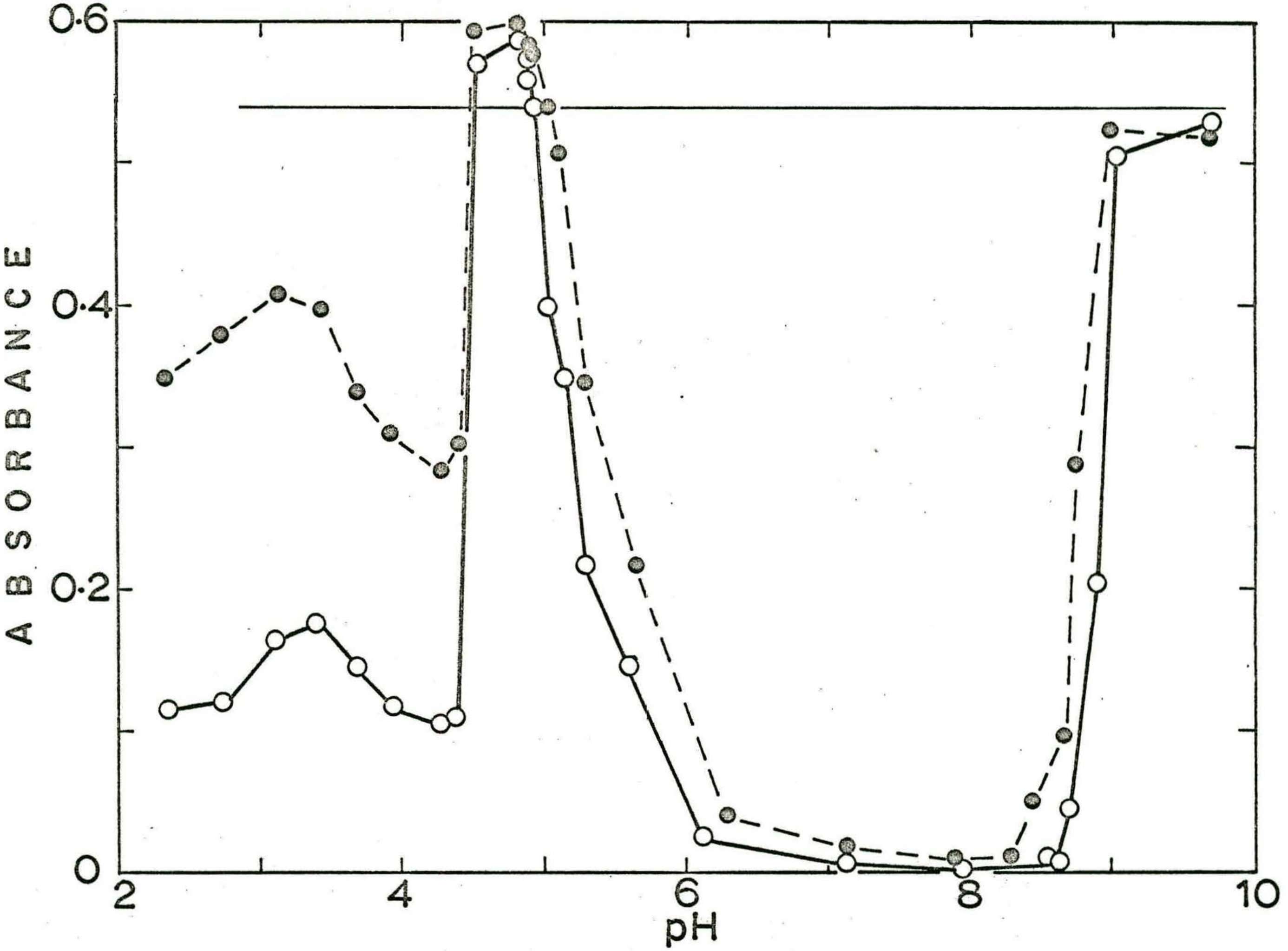

Figure 12. COAGULATION OF ILLITE BY 2.4 x 10^{-4} M $Al(SO_4)_{3/2}$. JAR TESTS.

Fast mix 10 minutes at 90 rpm. Blackened and open circles respectively show measurements taken after 5 and 20 minutes of slow mix.

blank sample (solid horizontal line). When the aluminum concentration was lowered to 7.08 x 10^{-5} M, as demonstrated by Figure 14, there was a significant drop in this maximum signaling the disappearance of this restabilization region. As shown in Figure 15 the disappearance is virtually complete at an aluminum concentration of 6.32 x 10^{-5} M. In general there was no discrete left boundary at low Al(III) concentration. At all concentrations of aluminum the slow coagulation region was present at low pH and the stability region was present at high pH. The restabilization zone was only present over a limited range of aluminum concentrations and then only between the slow and rapid coagulation regions.

Stability Domain for Illite

The critical pH values for coagulation (pH_c) and the critical pH values for stabilization (pH_s) obtained from absorbance-pH curves were plotted as a function of the logarithm of the corresponding aluminum concentrations. This plot, shown in Figure 16, is the "Log $Al(SO_4)_{3/2}$ Concentration-pH Domain of Stability for the Coagulation of Illite." It delineates regions of stability and coagulation for illite for any given pH and alum dose. The pH_c and pH_s values for the jar test runs are represented by circles while the pH_c and pH_s values for the "non-mixing" runs are represented by squares. Open symbols are coagulation data and blackened symbols are stabilization data. In these studies the steep parts of the curves constructed with the 20 minute slow mixing data were extrapolated to zero absorbance to obtain the values of pH_c and pH_s. The critical pH values obtained in the "non-mixing" studies were found to be compatible with the jar test values if the extrapolation was to the initial turbidity of the blank and if the 15 minute

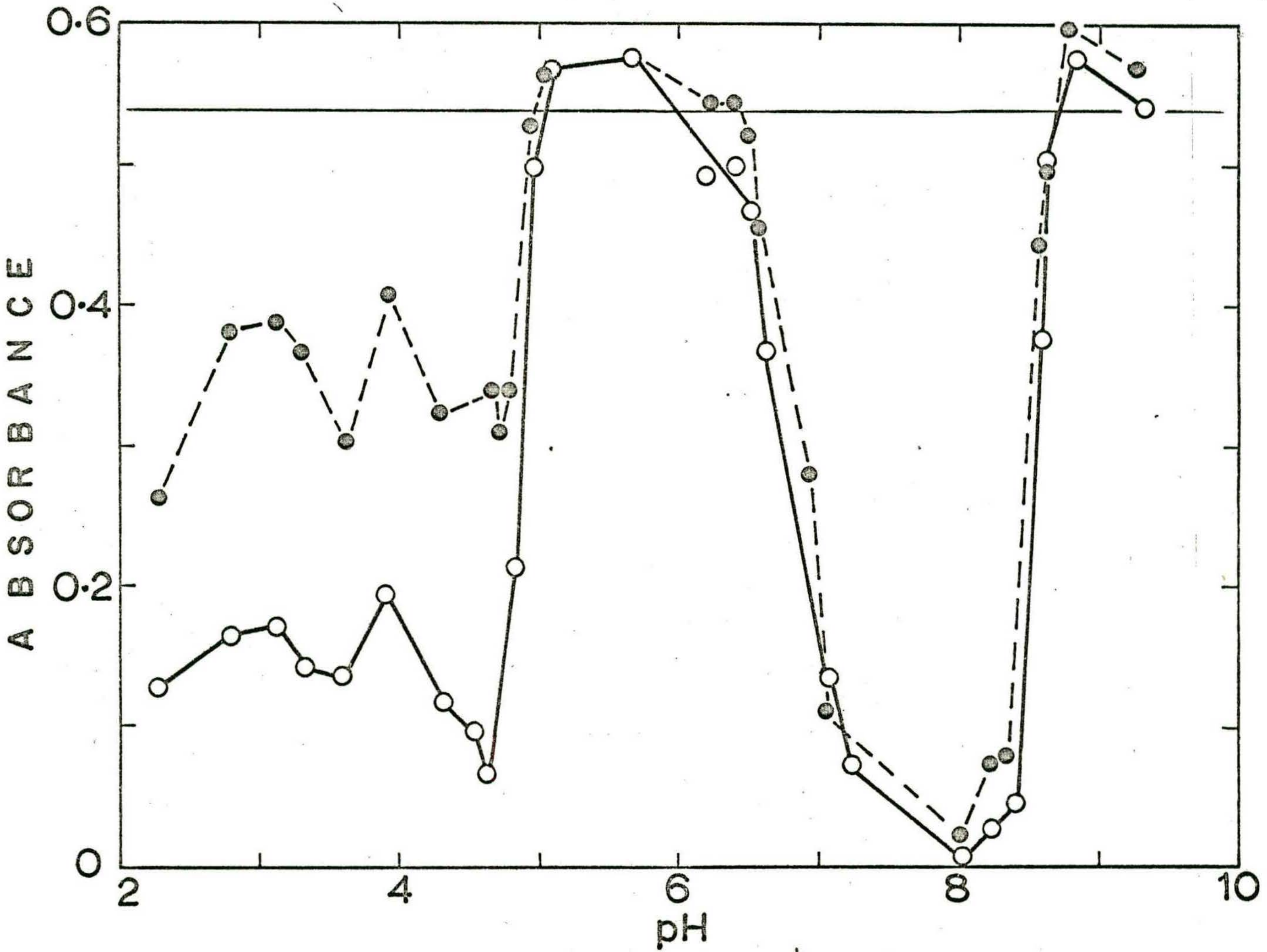

Figure 13. COAGULATION OF ILLITE BY 1.0×10^{-4} $\underline{M}$ $Al(SO_4)_{3/2}$. JAR TESTS.

Fast mix 10 minutes at 90 rpm. Blackened and open circles respectively show measurements taken after 5 and 20 minutes of slow mix.

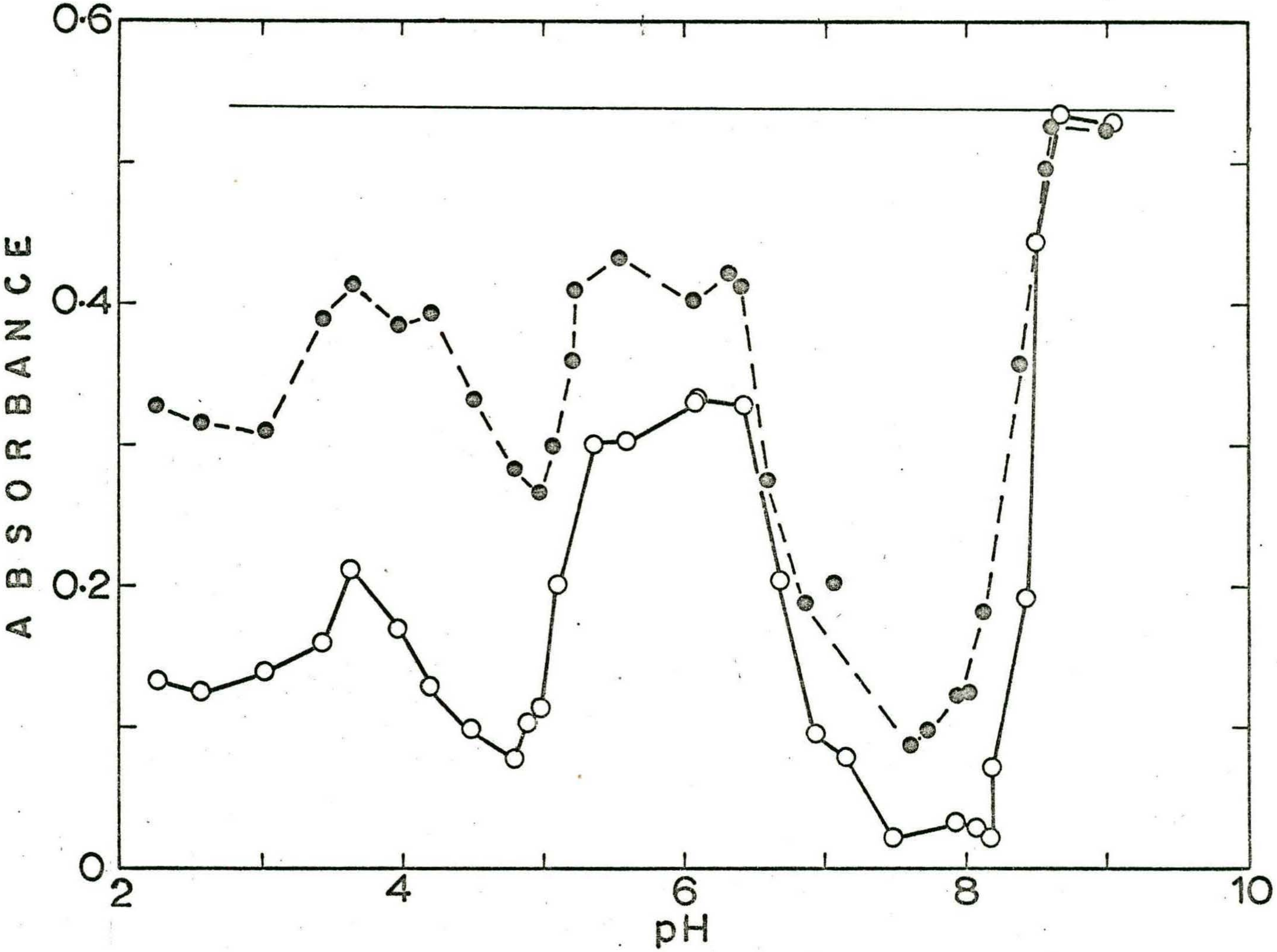

Figure 14. COAGULATION OF ILLITE BY 7.08 x 10^{-5} $\underline{M}$ $Al(SO_4)_{3/2}$. JAR TESTS.

Fast mix 10 minutes at 90 rpm. Blackened and open circles respectively show measurements taken after 5 and 20 minutes of slow mix.

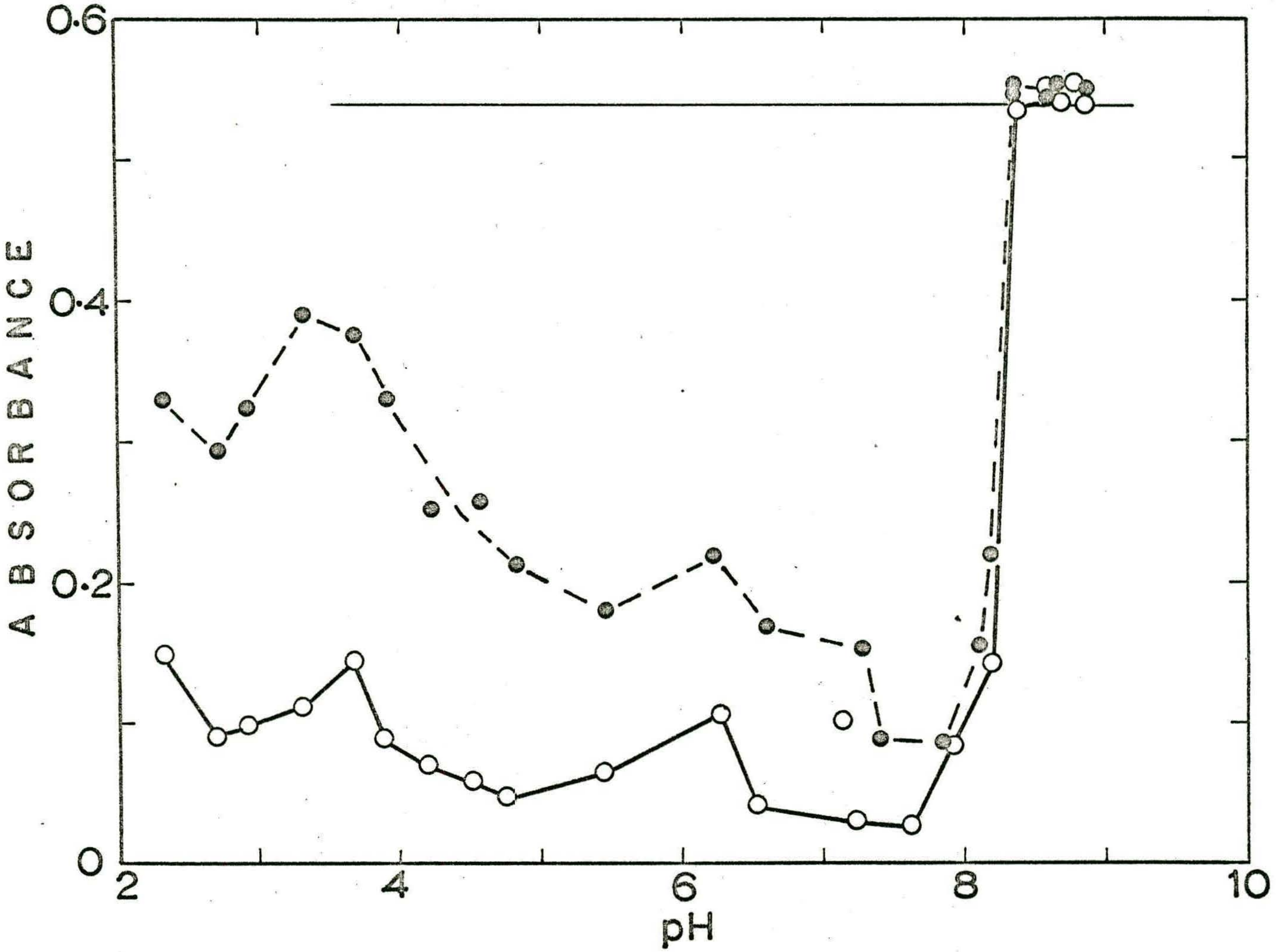

Figure 15. COAGULATION OF ILLITE BY 6.32 x 10^{-5} M $Al(SO_4)_{3/2}$. JAR TESTS.

Fast mix 10 minutes at 90 rpm. Blackened and open circles respectively show measurement taken after 5 and 20 minutes of slow mix.

absorbance-pH curves were used for extrapolation on the left of the "sweep zone" and if the 1 hour curves were used on the right.

The c.c.c. values are indicated by hexagons for the jar test runs and by diamonds for non-mixing runs. These represent the results obtained by varying the alum concentration at constant pH. This procedure is believed to be the most suitable for obtaining the lower limit of the coagulation zone.

The stability domain of illite is characterized by four distinct zones. A slow coagulation zone lies to the left and delineates the region in which hydrogen ions act as the coagulant. In the middle of the domain there is a wide "sweep zone" of aluminum precipitation and rapid settling which narrows downward before reaching its lower limit at a log $Al(SO_4)_{3/2}$ concentration of -4.5. This lower limit is also the critical coagulation concentration. To the right of the sweep zone and below it is located a zone of no coagulation where no appreciable reduction in turbidity had occurred by the end of the tests.

The boundary between the sweep zone and the slow coagulation zone is formed by a sloping straight line. An extension of this line also forms part of the boundary between the slow coagulation and the restabilization zones. The rest of the boundary is formed by another short line which apparently had a different slope. The sweep zone is also separated from the no coagulation zone in part by a long and sloping straight line. The no coagulation region also has a common boundary with the slow coagulation zone. This boundary is curving line of positive slope which starts from the level of the c.c.c. value and reaches the bottom boundary of the domain.

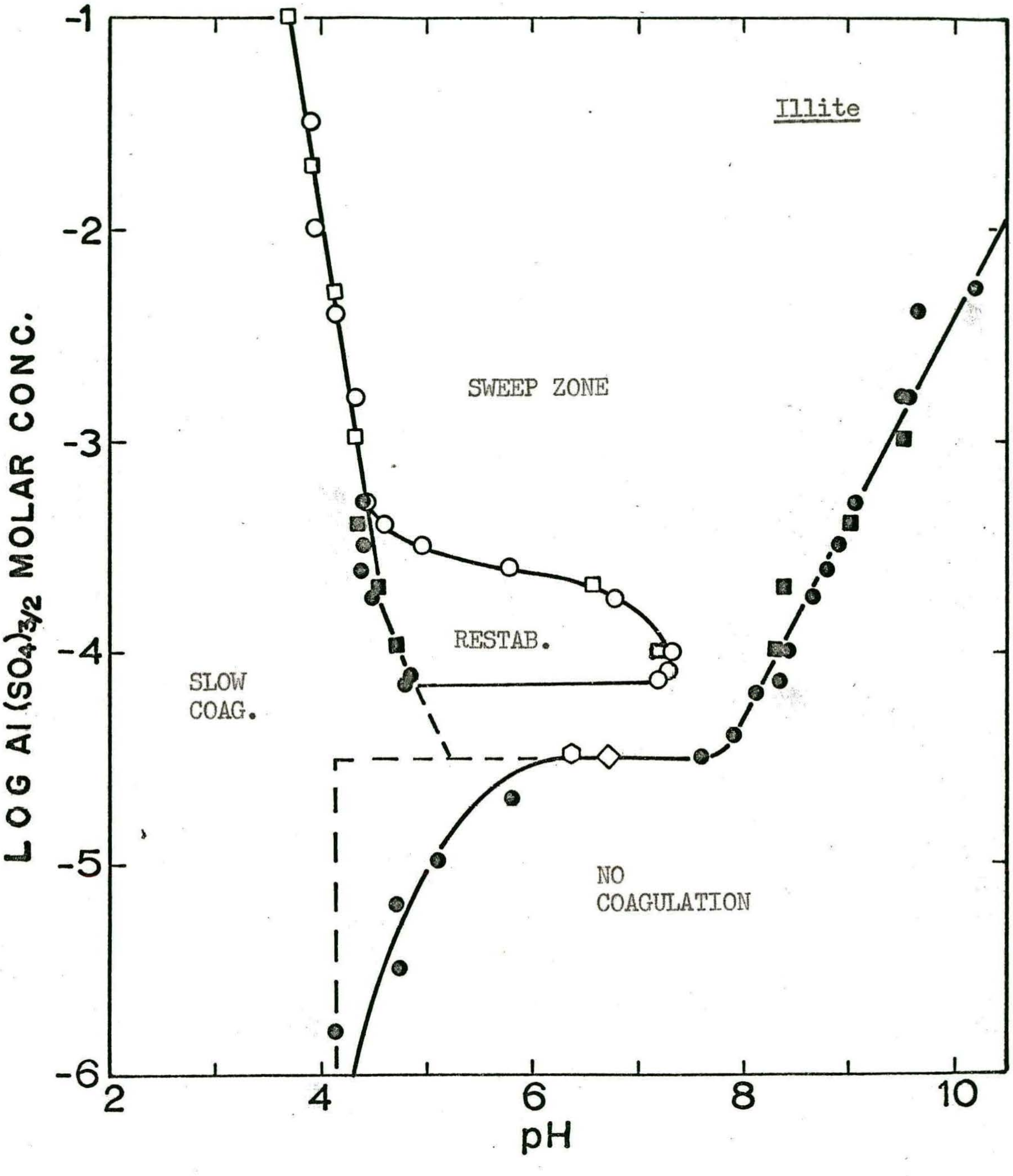

Figure 16. LOG ALUMINUM SULFATE CONCENTRATION-pH DOMAIN OF STABILITY FOR ILLITE.

Circles are jar test and squares are non-mixing coagulation results. Blackened symbols are pH_s values and open symbols are pH_c values. Open hexagon and diamond are c.c.c. values determined from jar test and non-mixing test respectively.

Chapter IV

DISCUSSION OF RESULTS

Comparison of Clays

The coagulation of illite, kaolin and montmorillonite was compared using the non-mixing technique. Kaolin appears to be unsuitable for a long term coagulation study because its suspensions are inherently unstable. Despite long periods of crushing in the ball mill followed by high speed blending, significant settling occurred in its suspensions after an hour. The addition of acid or base did not improve its stability. The instability is reflected in Figures 2 and 5. It was also peculiar to kaolin that restabilization at 1.0×10^{-4} $\underline{M}$ $Al(SO_4)_{3/2}$ endured for the 12-hour period of the test. In general illite suspensions were more stable than those of kaolin. Restabilization of illite at low concentrations of alum was also observed but stability persisted for less than 3 hours. Restabilization had the effect of raising the absorbance of the illite suspensions above the initial turbidity value. These were the only differences observed between kaolin and illite. The pH_c and pH_s for both clays at 1.0×10^{-4} $\underline{M}$ and 1.0×10^{-3} $\underline{M}$ $Al(SO_4)_{3/2}$ were approximately the same. Acid coagulation also occurred in similar pH ranges and at the same time.

Montmorillonite suspensions were the most stable requiring little crushing to disperse. At low pH acid coagulation occurred as soon as the reacting components were mixed. Therefore no slow coagulation region was present at the left of the absorbance-pH curve. The speed with which acid coagulation occurred suggested that direct chemical reaction might have been involved. There was no restabilization at 1.0×10^{-4} $\underline{M}$ $Al(SO_4)_{3/2}$ as was observed with the coagulation of illite and kaolin. Restabilization results from adsorption of more counter-ions than is necessary to neutralize the colloid's charge (38). Therefore the absence of restabilization means either that montmorillonite cannot adsorb excess aluminum cations or that there are insufficient cations available for the larger surface area of montmorillonite suspensions.

Comparison of Test Procedures

The results indicate that both the jar test technique and the non-mixing technique can effectively be used for studying coagulation. However there are some obvious advantages in using the jar test method with clays. It is less laborious and as modified for this study requires only a short period of 30 minutes. With non-mixing method, on the other hand, samples were allowed to settle for over 12 hours. Therefore interferences due to the inherent instability of the clays would not be as significant with the jar tests as they might be with the non-mixing tests. Also the jar test technique seems to give more reproducible absorbance-pH curves and consequently more consistent values of pH_c and pH_s. There are two plausible explanations for this. The first is that sampling and measurement errors are lessened because of the larger sample volumes employed with the jar test. Secondly, mixing may add to the reproducibility since fast mixing ensures even dispersion of the reactants and slow mixing allows aggregation to occur in a shorter time. The fast mixing steps have the further advantage of being more representative of coagulation in practice.

With the non-mixing technique the ideal requirement is that the sample remain in a state of quiescence after the initial mixing of components. This condition is not achieved because a pH electrode has to be inserted into the sample and also because the samples have to be moved for the absorbance measurements. To what extent these disturbances affect the results was not determined. There is little doubt, however, that they affect the rate of aggregation by introducing velocity gradients.

Coagulation of Illite

The results of the studies on the coagulation of illite are summarized in Figure 16. This figure is the entire domain of stability for the coagulation of this clay by aluminum sulfate. The results with illite indicate that in the slow coagulation zone the removal of turbidity was not influenced by the concentration of aluminum sulfate. Below pH 4.5 the general form of the absorbance-pH curves was the same for tests run with pH adjustment only and those run at all concentrations of aluminum sulfate. Coagulation in this zone must therefore be attributed to hydrogen ions only. With the non-mixing tests the absorbances were relatively constant over the acid range whereas with the jar tests a maximum in abosrbance was reached at approximately pH 3.5.

The boundary between the slow coagulation zone and the sweep zone was a straight line, the slope of which was found by least squares to be 3.2. The line is similar to the line obtained in the coagulation of bacteria (15).

Clarification was most efficient and rapid in the sweep zone. As shown in Figures 1 and 4 a high degree of turbidity removal was obtained even without the aid of slow mixing. Since the volume of the floc was much greater than that of the dispersed clay alone, the predominant mechanism of clarification in this zone must be the enmeshment of the clay particles by the aluminum "hydroxide" precipitate. The diagonal boundary between the sweep zone and the zone of no coagulation was found to be straight line of slope 0.98 and intercept -12.2. Rubin and Hanna (35) and Hanna (15) showed that this line represented the solubility line determined by the equilibrium condition:

$$Al(OH)_{3(s)} + H_2O = Al(OH)_4^- + H^+$$

The log K_s for this equilibrium is -12.7 and the exact slope of the solubility line is 1. The sweep zone is definitely limited by the above equilibrium relation. Therefore the sweep zone is limited on the left and right by the solubility of aluminum "hydroxide" precipitate.

The restabilization zone is bounded on the left partly by an extension of the boundary between the sweep zone and the slow coagulation zone and partly by a straight line having a slope of 1.1. The other boundaries of the zone are curved lines. In the coagulation of silver iodide Matijevic and Stryker (23) reported that restabilization was due to reversal of charge by the adsorption of highly charged hydrolyzed aluminum species. They proposed that the reversing cation was $Al_8(OH)_{10}(SO_4)_5^{4+}$. This in turn predicts an exact slope of 1.25 for the left boundary of the restabilization zone. The value of 1.1 is sufficiently close to their prediction.

Restabilization has been reported as leading to an increase in turbidity. This increase could be due either to particle growth of the clay particles or the presence of aluminum precipitate. The results indicate this increase must be due to the formation of restabilized aluminum precipitate. The eventual settling of the restabilized particles as indicated in Figure 4 is most likely due to coagulation by sulfate anions. Coagulation below the restabilization zone is believed to occur because of reduction in the magnitude of the reversed charge. Packham (29) plotted the zeta potential of kaolin in aluminum sulfate solutions against pH and found that in the areas where the charge was reversed the magnitude of the charge decreased with decrease in aluminum sulfate concentration.

The critical coagulation concentration obtained for illite at pH 6.7 was 3.1×10^{-5} $\underline{M}$ $Al(SO_4)_{3/2}$. Various possible aluminum species were assumed to be the limiting species for coagulation and the c.c.c. of sodium nitrate and calcium nitrate were used to plot the graph of log (c.c.c.) versus their ionic charges. For the various species assumed these attempts failed to produce a straight line plot in accordance with the Schulze-Hardy rule. Therefore coagulation of illite by aluminum sulfate does not follow the Schulze-Hardy rule. Considering that Packham (28) has indicated that the concentration of dissolved aluminum sulfate in the pH range of 5.5 to 7.5 is less than 1.0×10^{-6} $\underline{M}$ the value of 3.1×10^{-5} $\underline{M}$ for the c.c.c. also implies that precipitate is present at the c.c.c.

The left boundary of the zone of no coagulation at the lower part of Figure 15 departs noticeably from the results with the coagulation of bacteria (15). A curved line is shown here whereas a vertical line was obtained in the coagulation of bacteria. The vertical dashed line to the left of the curved line indicates the expected boundary for H^+ ion coagulation. Between the two lines true coagulation must be occurring. The curvature of this boundary line is hard to explain. It may be that in the pH range it covers, the proportion of ionic species is rapidly varying with pH.

Future Work

A number of further investigations have been suggested by this research:

1. Electropheris studies should be conducted to determine the sign and magnitude of the surface charge on the clay and precipitate at various points in the domain.

2. An attempt should be made to isolate the aluminum precipitates from the suspensions by dialysis so that the value of the c.c.c. in the absence of aluminum precipitates may be determined and compared with the value obtained in this study.

3. Ultracentrifuge studies should be used in combination with schlieren measurements in an attempt to locate the lower limits of precipitation.

Summary of Conclusions

Based on the experimental results the following conclusions are indicated:

1. a. A straight line could not be obtained by plotting the log (c.c.c.) of the neutral salts and alum against the counterion charges in spite of the fact that all possible whole number charges were assumed for the aluminum species.

b. The c.c.c. value for alum was far in excess of the amount of dissolved aluminum expected at the pH of the sample.

Therefore it is concluded that the coagulation of illite by aluminum sulfate under the experimental conditions employed does not follow the Schulze-Hardy rule, and that coagulation in the neutral pH range was not controlled by the concentration of a charge bearing aluminum species.

2. a. The ordinate intercept of the straight line boundary between the sweep zone and the zone of no coagulation is 12.2 which approximates the $K_{equil.}$ for $Al(OH_3)\ (s) = Al(OH)_4^- + H^+$.

b. Also the slope of this line is approximately one.

Therefore clarification at high pH is limited by the formation of soluble aluminate ion.

Apparently, the mechanics of clarification in the neutral pH zone is due to enmeshing by insoluble aluminum precipitate.

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