SUMMARY

The pressor response to 1-phenyl-2-hydrazino-propane is essentially the same in hypertensive as in normotensive dogs.

The cardiac rate decrease which accompanies the blood pressure elevation following the administration of this compound does not occur in atropinized dogs.

The pressor response to 1-phenyl-2-hydrazino-propane is completely blocked by phentolamine, indicating the absence of a musculotropic component and the involvement of the sympathetic pathway in the response.

The pressor response to this compound is not affected by the prior administration of hexamethonium, making unlikely the possibility of ganglion and central stimulation.

The diminution of the pressor response to 1-phenyl-2-hydrazinopropane in reserpinized dogs
and those which had received guanethidine gives support to the combined mechanism at the myoneural junction of direct and indirect effector cell receptor site stimulation, the latter by MAO (or other enzyme) inhibition or by the peripheral release of catecholamines in the blood vessel walls.

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Phase Solubility Study of Solid Species Formed by Magnesium Aluminate from Aqueous Solutions Containing Sulfate Ions

By TAKERU HIGUCHI and FOO SONG HOM†

A phase solubility technique has been used to detect and establish the nature of several hydrated solid species formed by sulfated magnesium aluminate. The most stable form at lower magnesium level appears to correspond to a hydrate of $4MgO : Al_2O_3 : SO_3$. Equilibrium behavior of this substance is such as to obey the solubility product principle with regards to both magnesium and sulfate. Under other conditions species corresponding to $MgO:Al_2O_3$, $3MgO : Al_2O_3 : SO_3$, and $8MgO:Al_2O_3 : SO_3$ seem to be produced. The results demonstrate the great value of the phase solubility technique in studying complex inorganic systems.

SERIOUS INVESTIGATIONS of the physical states of precipitated hydrous oxides and mixed hydrous oxides have been severely limited by the instability of these inorganic systems and by the difficulty in establishing their true states and compositions without washing or drying. For this reason, despite wide pharmaceutical usage of many of these compounds as bases for antacids, no detailed physical-chemical studies on these systems have been published in recent years. The present report is concerned with the results of an investigation on a hydrous sulfated magnesium aluminate system which makes use of

a phase solubility technique developed earlier for studies on formations of organic complexes. The data presented show that the $mMgO \cdot nAl_2O_3 \cdot pSO_3 \cdot xH_2O$ systems could exist in a number of different stoichiometric ratios.

Results of the present studies suggest that formations of distinct solid species having the following approximate compositions are favored by hydrated aluminum and magnesium oxides in contact with aqueous solutions containing sulfate ions: (a) $3MgO \cdot Al_2O_3 \cdot SO_3 \cdot xH_2O$, (b) $4MgO \cdot Al_2O_3 \cdot SO_3 \cdot yH_2O$, and (c) $8MgO \cdot Al_2O_3 \cdot SO_3 \cdot zH_2O$. The presence of sulfate in the structure appears to be necessary. These systems appear to possess distinct solubility products based on the concentrations of the three components.

These findings also attest to the value of phase solubility determinations in the detection and

characterization of complex inorganic species. No other technique at the moment can give such unequivocal evidence of formation of these discrete phases.

PAST WORK

Interactions of aluminum and magnesium oxides in more or less their hydrated state to form complex species have received serious attention by numerous previous workers (1–17). In many instances no more was claimed than that an amorphous mixture of improved therapeutic value as an antacid was claimed. In other cases there were evidences for formation of discrete solid phases.

The work of Hallman (12) is of particular interest because of its close relationship to the present study. He claimed preparation of a hydrated magnesium aluminate species from strongly alkaline aluminate solution (pH 12–13) and magnesium sulfate having the following formula

$$[Mg(OH)]_4 \, [(HO)_4Al \, {OH \atop OH} \, Al(OH)_4]$$
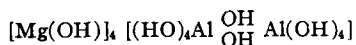
The work of Cole and Hueber (11) indicated that aluminate concrete long exposed to sea water formed $4MgO \cdot Al_2O_3 \cdot xH_2O$ and $4MgO \cdot 2Al_2O_3 \cdot MgSO_4 \cdot xH_2O$.

In general, the past studies suffered from the fact that compositional determinations were based on analysis of washed samples of the precipitated phases. Since many of these systems were subject to hydrolytic changes during washing, these analytical findings did not reflect the actual composition of the precipitates. For the present investigations, use was made of the phase solubility technique developed earlier for systems of this type (18) which permitted determination of the true nature of the precipitated phase.

EXPERIMENTAL

Reagents

Only reagent grade chemicals were used except for the indicators which were utilized as received. The water used in these studies was made by distillation from all borosilicate still of ordinary distilled water. For phase solubility studies this was boiled and cooled under nitrogen prior to use.

Preparation of Sodium Aluminate Solution.—The formula used for 0.2 M stock solution was: $Al(OH)_3 \cdot nH_2O$ (Fisher Scientific Co.), 15.22 Gm., sodium hydroxide, reagent grade, 25.00 Gm., and enough distilled water to make 1000 ml.

Procedure.—The sodium hydroxide was heated in a nitrogen atmosphere to a melt in a large nickel crucible. Aluminum hydroxide was added with stirring to the melt in small divided portions with a nickel spatula. After completion of the addition, the mixture was stirred thoroughly and cooled to room temperature under nitrogen. About 100 ml. of distilled water was added to the resulting sodium aluminate and heated to effect complete solution. The solution was allowed to cool and was made to one liter with distilled water and stored in a polyethylene bottle.

Methods of Analysis

Gravimetric Determination of Aluminum (19)

and Magnesium.—The method is based on the fact that aluminum forms an insoluble complex ($pK_{sp} = 29.0$) with 8-hydroxyquinoline quantitatively in the pH range of 5 and 10, whereas the magnesium complex is insoluble and forms only in alkaline pH, preferably 10. Thus, this method can be used to determine aluminum, in the presence of magnesium, and magnesium as well.

Procedure.—The sample containing aluminum and magnesium (10 to 50 mg. of each) was acidified with hydrochloric acid in a 400-ml. beaker. To this solution was added 5 to 10 ml. of 10% tartaric acid solution (10 × wt. of aluminum) to keep the aluminum in solution, followed by 15 ml. of a 30% ammonium acetate solution. After dilution with distilled water to 300 ml., the pH was adjusted with 2 N ammonia to 5.2 to 6.8 with the aid of 3 drops of a bromocresol purple indicator solution. The solution sample was warmed, and then 5 ml. of a 50% 8-quinolinol in glacial acetic acid was pipetted into the beaker with stirring. Four or five milliliters of isopropanol was added in some instances to help contain the precipitate in the beaker. The system was heated to nearly boiling and allowed to digest from 0.5–1.0 hour at the temperature of the steam bath, or until the precipitate had become hard and crystalline. During the process of digestion, if the supernatant solution turned pale greenish yellow, more precipitant was added until it turned a definite yellowish orange. At this time the system was cooled to 60° and filtered into a tared 30-ml. glass crucible fitted with a fritted disk of medium porosity. The precipitate was washed with about 75 ml. of distilled water and dried at 135–145° to constant weight (about 2–4 hours). After cooling for one hour in a desiccator, the precipitate was weighed as the anhydrous complex with a molecular weight of 459.42 Gm. per mole.

The determination of magnesium was carried out by collecting the filtrate and the washings from the aluminum determination and placing it into a 600-ml. beaker to which were added 25 ml. of strong ammonia (to give pH 10) and 5–15 ml. of saturated 8-quinolinol in isopropanol. The remaining procedure was the same as given above, except that the precipitate was washed with a 30% isopropanol solution containing 1% ammonia. The precipitate was weighed as the anhydrous complex with a molecular weight of 312.60 Gm. per mole.

EDTA Titration of Magnesium.—The direct titration of magnesium in solution presented no difficulties except that the rate of reaction between EDTA and magnesium-Eriochrome Black T complex (20, 21) and magnesium-Calmagite complex was rather low at room temperature. To overcome this difficulty, the titration was carried out at 60°. Even though Lindstrom and Diehl (22) claimed that Calmagite was more stable than Eriochrome Black T when both were 0.1% aqueous solutions, these indicators were best used as 1% triturations in either sodium chloride or potassium chloride and stored in well stoppered bottles.

Lewis and Melnick (23) studied the accuracy in the determination of calcium and magnesium with EDTA and found that the magnesium titration at pH 10 was complete when a permanent blue color developed. When this end point was used, a satisfactory agreement was obtained for EDTA solutions standardized separately with four different

elements, the results agreeing within about one part per thousand.

Procedure.—A 5.0- to 25.0-ml. sample of the magnesium solution was pipetted into a 125-ml. Erlenmeyer flask and sufficient double distilled water was added to give a 45-ml. total volume. This was followed by 5 ml. of 0.1 M borate pH 10 buffer solution and heating on steam bath to 60°. After addition of an estimated 10–15 mg. of the indicator trituration, the sample was titrated slowly until all traces of the red tint had just disappeared and a permanent blue color appeared. The amount of magnesium was calculated: one ml. 0.0100 M EDTA = 0.2432 mg. of magnesium.

Precipitation of Sulfate as Barium Sulfate.— The method was that described by Blaedel and Meloche (24), but was tested for accuracy and precision in the experimental concentration range. The result for the average of four determinations of a 5.000×10^{-3} mole per liter of sodium sulfate solution was $4.99 \pm 0.05 \times 10^{-3}$ M.

Special Equilibration Procedure
Used in the Phase Studies

Short Equilibration Procedure—Beaker Method for Determining Acetic Acid Requirements.—A twenty-milliliter aliquot of the 0.1 M sodium aluminate solution was pipetted into a 150-ml. beaker containing a teflon encased magnetic bar and distilled water (sufficient to make up to approximately 100 ml. final volume) in a nitrogen atmosphere. To this was added with constant stirring 8.71 ml. of 1.042 N acetic acid containing varying amounts of 0.2 M magnesium sulfate. The final pH was measured after the system had apparently approached a steady value (about one-half hour). The precipitate was then quantitatively transferred onto a 60-ml. fritted disk glass filter, and washed with 75 ml. of distilled water. The precipitate was dissolved with sufficient concentrated hydrochloric acid and followed by several portions of distilled water. The filtrate was collected in a 400-ml. beaker. The aluminum and magnesium contents of the filtrate were determined by the 8-quinolinol precipitation method.

Long Equilibration Procedure Bottle Method for Determining Acetic Acid (or Sodium Hydroxide) Requirement.—Preliminary potentiometric titrations served as guides in spacing the amount of 0.1 M acids or acidic compounds to be used. The preselected volume of 0.1 M titrant was accurately measured into a 120-ml. wide mouth bottle equipped with a polyethylene lined screw cap. Sufficient distilled water was added to give 95.0 ml. before 5.0 ml. of the 0.1 M sodium aluminate solution was added from a 10-ml. autoburet to give the 100-ml. final volume. After the cap was secured on tightly, the system was equilibrated by slow rotation in a constant temperature bath set at 30° for two days or longer. At the end of this period the bottles were allowed to stand overnight in the bath to permit the fine precipitates to settle leaving a clear supernatant liquid. The screw cap was removed after careful drying and the pH of the supernate was measured.

Bottle Method—Phase Study of Unbuffered Systems.—The predetermined amounts of distilled water, 0.1 M sodium sulfate, 0.1 M acetic acid, or 0.1 N sodium hydroxide (as necessary to yield the approximate final desired pH value), 0.1 M mag-

nesium acetate, and 0.1 M sodium aluminate solution were measured accurately in order as listed into a 120-ml. bottle to give a total final volume of 100 ml. A series of such bottles was prepared at one time. These prepared samples were rotated at 30° for a period of five days or longer at 30 r.p.m., after which time the same procedure was followed as given in the preceding section. Mixtures containing definite precipitates were filtered through sintered glass filters, whereas those containing colloidal particles were filtered through membrane filters of appropriate pore sizes. The highest pH value attainable after a little agitation was recorded as indicated by a glass electrode. Aliquot portions of the solutions were taken for chelometric determination of magnesium and gravimetric analysis of sulfate.

Bottle Method—Phase Study of Buffered Systems.—The procedure used was essentially the same as for unbuffered systems except that part of the distilled water was replaced by a buffer solution. Either 0.1 M acetic acid or 0.1 N sodium hydroxide solution was used to adjust the system approximately to the desired pH before buffering at this pH. The volume of the buffer was such that when diluted to the final volume of 100 ml. the resulting solution gave the desired pH reading. The buffers consisted of either 0.2 M of ammonia or 0.2 M of tris-(hydroxymethyl)-aminomethane with various amounts of 0.2 M hydrochloric acid.

EXPERIMENTAL OBSERVATIONS

Results of experimental studies on hydrous magnesium aluminate systems formed in the presence of sulfate, acetate, and sodium ions are reported. In general, the methods of investigations utilized solu-
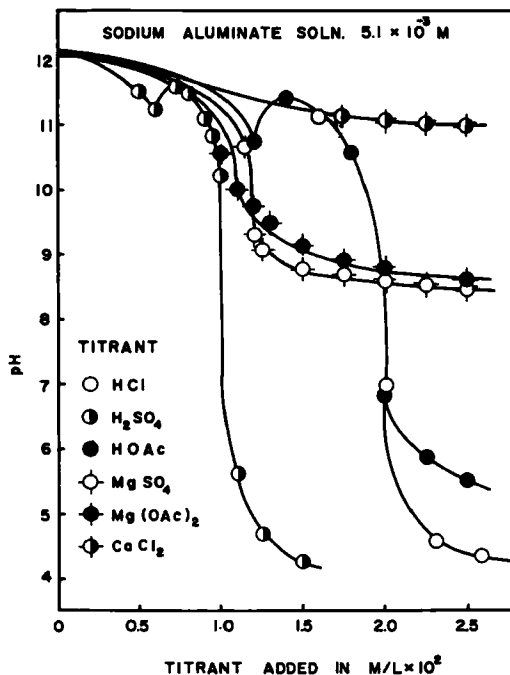

Fig. 1.—Changes in pH of a sodium aluminate solution containing an excess of sodium hydroxide as elicited by several acids and acidic salts.

TABLE I.—PHASE SEPARATION IN THE TITRATION
OF SODIUM ALUMINATE SOLUTION BY VARIOUS ACIDS
AND ACIDIC SALTS

Titrant	Gross Appearance	Max. pH
HCl	Pptn.	11.2
HOAc	Pptn.	11.4
H_2SO_4	Pptn.	11.6
$MgSO_4$	Pptn.	11.9
$Mg(OAc)_2$	Pptn. colloid	11.9
		11.8
$CaCl_2$	Pptn.	11.9

tions of sodium aluminate, magnesium sulfate, magnesium acetate, and acetic acid to achieve the desired end states. Preliminary investigations necessary in obtaining the proper ratios of reactants to yield systems having comparable end pH values are reported initially.

pH and Acid-Base Relationship

Changes in pH of Sodium Aluminate Solution Elicited by Slow Addition of Acids and Acidic Salts.—Because of its amphoteric nature, aluminum can exist in solution under either highly alkaline or acidic conditions. If a highly alkaline aluminate solution is progressively made acidic by additions of acids or acidic salts such as magnesium sulfate, magnesium chloride, magnesium acetate, or calcium chloride, aluminum is precipitated simultaneously as the pH decreases. Hence, a considerable insight into the mechanism of the precipitation process can be gained from such potentiometric titration plots.

Figure 1 shows the titration characteristics of a sodium aluminate solution (containing an excess of sodium hydroxide with a mole ratio of NaOH:Al (OH)₃ of approximately 3.9) when titrated with hydrochloric acid, acetic acid, sulfuric acid, magnesium sulfate, magnesium acetate, and calcium chloride. The bottle technique for potentiometric titration under equilibrium conditions was utilized in obtaining these results. Each bottle contained 0.51 mmole of aluminate plus a definite quantity of titrant (varying in the series of bottles) in a total volume of 100 ml. The systems were equilibrated at 30° for two days, after which the pH of the supernatant liquid was determined by use of an alkaline range glass electrode.

Potentiometric titration at a normal rate of addition of 0.1 N sulfuric acid under a nitrogen atmosphere produced erratic pH readings with considerable drift in values. This phenomenon may be explained by the fact that aluminum can exist in aqueous solutions, depending on the medium, in several different forms of aquo-hydroxy species. A change in the medium necessitates a readjustment of the involved equilibria in accordance with the mass law. For this reason the potentiometric readings were obtained under at least pseudoequilibrium conditions.

From the plots depicted in Fig. 1 it is evident that in the highly alkaline pH range both acids and magnesium salts were effective in depressing the pH and in precipitating the aluminate solution. The maximum pH values at which the solid phase just appeared in each system are given in Table I.

Change in pH Produced by Fast Addition of Magnesium Sulfate to Sodium Aluminate Solu-

tion.—The effect on the hydrogen ion concentration elicited by different rates of incremental addition of magnesium sulfate to the sodium aluminate solution is clearly evident in Fig. 2. In the beaker method potentiometric readings were taken approximately thirty minutes following the addition. In the bottle method, pH determination was made after two days of equilibration under constant agitation. In all cases the system contained a total of four mmoles of aluminum.

The longer equilibration period gave a much sharper potentiometric break. It also produced markedly greater degrees of precipitation of aluminum at higher pH values, nearly all of the trivalent element being removed from solution by the bottle procedure at pH 11, whereas very little precipitation occurred at this pH by the beaker method. This difference may be due to several factors, one of which is the gradual hydrolysis of the aluminate ion (which hydrolyzes slowly in aqueous alkaline solutions). Another possibility is that the sulfate ions may slowly exchange with the hydroxyl ions in forming a new solid phase, thus raising the pH. By both procedures, however, it would appear that nearly all aluminum is precipitated at pH of 8.5.

Acetic Acid Required to Attain Fixed pH in Formation of Hydrous Magnesium Aluminate in Presence of Sulfate.—In forming hydrous magnesium aluminate in presence of sulfate ions from sodium aluminate, acetic acid was used to neutralize the excess sodium hydroxide and to adjust the system to give an essentially constant final solution
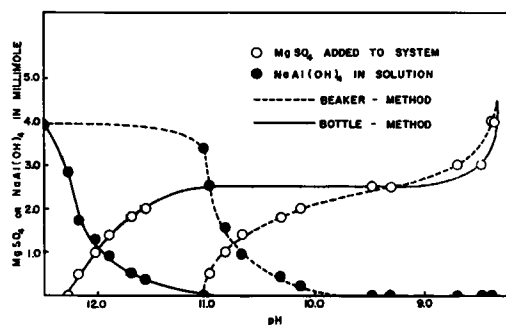

Fig. 2.—Difference in behavior between the beaker and the bottle methods for the precipitation of aluminate by magnesium sulfate as a function of pH.
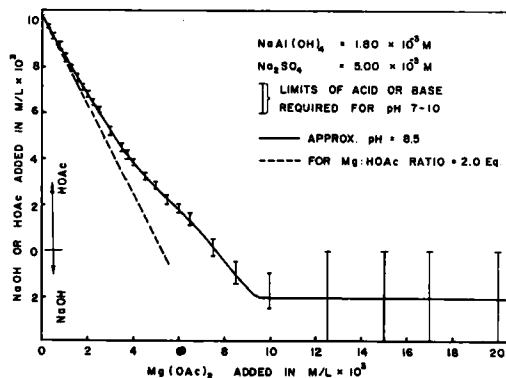

Fig. 3.—Acetic acid or sodium hydroxide–magnesium acetate relationship in systems containing aluminate and sulfate.

pH. It was desirable to maintain the hydrogen ion concentration by addition of acetic acid somewhat above that necessary to prevent precipitation of a discrete magnesium hydroxide phase (*ca.* pH = 10). For this purpose the amount of the acid needed to attain an approximate pH of 8.5 was determined for a system containing a fixed amount of sodium aluminate, sodium sulfate, and varying amounts of magnesium acetate. The bottle method was used, and the system was equilibrated for five days or longer at 30° before the pH of the clear supernatant liquid was determined.

Figure 3 gives the amount of acetic acid or sodium hydroxide added in moles per liter to yield an approximate final pH of 8.5 for various amounts of added magnesium acetate in a system containing 1.80×10^{-3} moles per liter of aluminate. It is evident again that in this pH range the amount of required acid is progressively decreased by addition of magnesium ions. The dotted line corresponds to a stoichiometric ratio of magnesium ion to acetic acid of 2.0. Although magnesium hydroxide is not precipitated as such, it would appear that at low magnesium ion concentration it becomes bound effectively as the oxide to the aluminum system to release two equivalents of hydrogen ions. The same intensity of magnesium ion binding appears to persist up to about two molar equivalents of aluminum present $(2 \times 1.80 \times 10^{-3} M = 3.60 \times 10^{-3} M)$. Beyond this point the binding tendency appears to decrease but still persists noticeably until approximately 12.6×10^{-3} moles per liter of hydrogen ions are released from 1.80×10^{-3} moles per liter of aluminate in the presence of excess magnesium ions $\left(\dfrac{H^+}{Al} = 7.0\right)$.
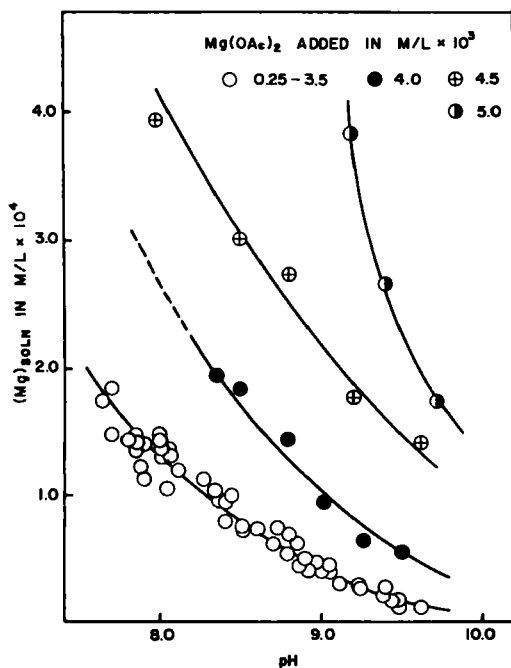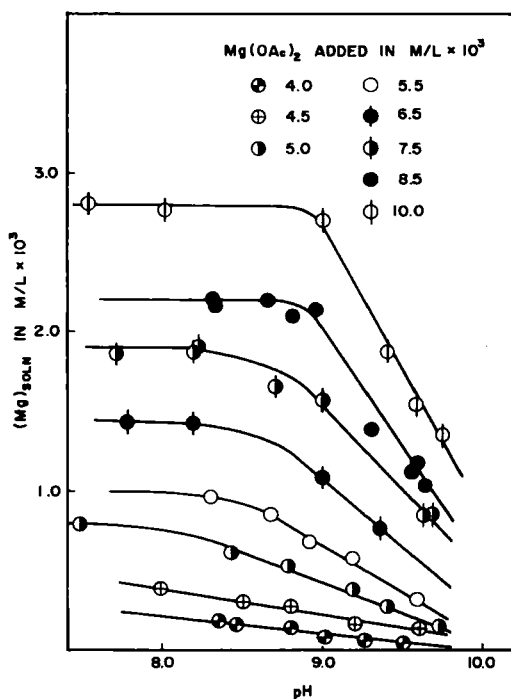
Fig. 5.—Changes in residual magnesium ion concentration in solution elicited by 1.80×10^{-3} *M* aluminate as a function of pH for several values of added magnesium acetate in presence of 5.0×10^{-3} *M* sodium sulfate.

Phase Solubility Studies on Unbuffered Systems

For the system involving formation of complex crystalline hydrated magnesium aluminate species from solutions of sodium aluminate, magnesium acetate, sodium sulfate, and acetic acid (or sodium hydroxide), considerable information relative to the roles played by each component can be obtained from phase solubility diagrams of various types. In the succeeding sections the influence of concentration of individual components on the extent of reaction of others are reported. All of the studies were carried out under conditions permitting establishment of equilibrium or pseudoequilibrium relationships.

pH and Degree of Magnesium Ion Binding.— Figures 4, 5, and 6 show the extent of magnesium ion binding exhibited by 1.80×10^{-3} *M* aluminate solution containing 5.0×10^{-3} *M* sodium sulfate. Figure 4 covers the range of added magnesium acetate of 0.25–5.0×10^{-3} *M;* Fig. 5 from 4.0–10.0×10^{-3} *M* and Fig. 6 from 12.5–20.0×10^{-3} *M*. The pH values were those obtained by the addition of appropriate amounts of acetic acid or sodium hydroxide. Any reduction in solution concentration below the slope of one is, of course, due to binding in these plots.

The data interpolated from the plots were used to construct Figs. 7 and 8. These phase solubility diagrams can be interpreted in terms of the classical phase rule. According to Fig. 7, the presence of less than the atomic ratio of Mg:Al of 2.0 led to essentially an invariant concentration of magnesium ion in the supernatant liquid, suggesting the presence of two discrete solid phases over this plateau
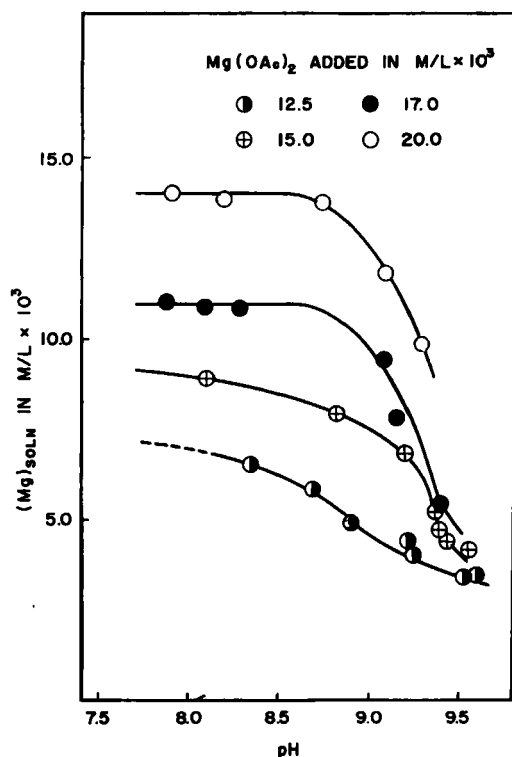
Fig. 4.—Changes in residual magnesium ion concentration in solution elicited by 1.80×10^{-3} *M* aluminate as a function of pH for several values of added magnesium acetate in presence of 5.0×10^{-3} *M* sodium sulfate.

Fig. 6.—Changes in residual magnesium ion concentration in solution elicited by 1.80×10^{-3} M aluminate as a function of pH for several values of added magnesium acetate in presence of 5.0×10^{-3} M sodium sulfate.

range. An increase in the added magnesium concentration above this point (3.60×10^{-3} M) resulted in a sharp rise in the magnesium ion concentration in solution. The slope at this point was, however, well below one. Further increase in the amount of added magnesium ion eventually caused a corresponding rise in solution concentration as shown in Fig. 8. Each dotted line extrapolated to a solid phase with an atomic composition of four magnesium to one of aluminum.

The influence of pH on the phase solubility diagrams was noticeable but surprisingly small. This was particularly true at pH values below 9 and with higher added magnesium acetate concentrations.

The results presented were obtained by use of the bottle method as described in the section on experimental procedure for phase solubility studies in unbuffered systems. Predetermined amounts of the components were added to each bottle in a definite order. The aluminate solution used contained a large excess of sodium hydroxide with a sodium hydroxide to aluminum hydroxide molar ratio of approximately 5.7. The systems were equilibrated at 30° for five days or longer after which the pH and the magnesium concentration in the supernatant liquid were determined.

In summary, the phase solubility diagrams obtained have indicated formations of at least two crystalline forms of $m\text{MgO} \cdot n\text{Al}_2\text{O}_3 \cdot p\text{SO}_3 \cdot x\text{H}_2\text{O}$. The first had an atomic ratio of Mg:Al of 2.0 and the second had a ratio of 4.0. The very flat plateau corresponding to the formation of the first suggested

that the structure of this species was such as to permit ready formation of well-defined crystals. On the other hand, the second corresponded possibly to a limiting structure where definite crystals formed but might have permitted partial replacement by magnesium ions. Only in the limiting case would the ratio of 4.0 be achieved.

Effect of Sulfate Concentration on the Degree of Magnesium Binding.—A review of Table I indicates that sulfate was necessary in the formation of solid phases in reactions of magnesium ion with aluminate. The reaction between magnesium acetate and sodium aluminate invariably produced a colloid which could be coagulated, besides sulfate, by many other polyvalent anions. For this reason sulfate was used in excess but constant amount (5.0×10^{-3} M) in the previous phase solubility studies.

Some experimental data to show the effect of added sulfate concentration on the degree of magnesium binding exhibited by 1.80×10^{-3} M aluminate for three initial magnesium acetate values have been compiled in Table II. Figure 9 gives the plot of magnesium solution concentration vs. the amount of added sodium sulfate and the colloid-precipitation range as well. Figure 10 shows the reciprocal relationship of added sodium sulfate concentration on the degree of magnesium binding for three values of added magnesium acetate. Although the pH values of these systems ranged rather widely, the averages were 8.6, 8.7, and 8.6 for the
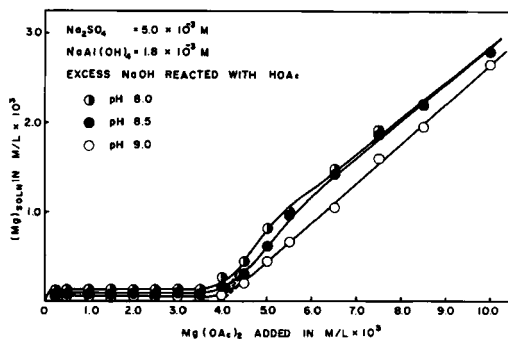

Fig. 7.—A phase solubility diagram showing the degree of magnesium ion binding exhibited by aluminate in presence of sulfate for three pH values.
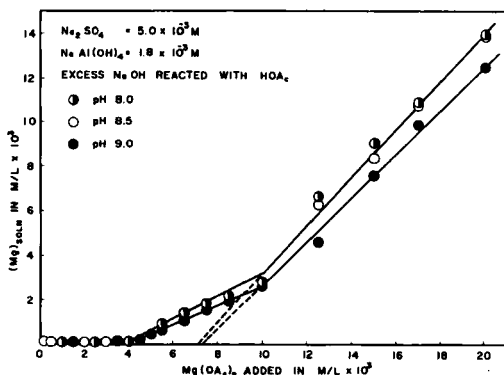

Fig. 8.—A phase solubility diagram showing the degree of magnesium ion binding exhibited by aluminate in presence of sulfate for three pH values.

TABLE II.—EFFECT OF SULFATE CONCENTRATION
ON THE RESIDUAL CONCENTRATION OF MAGNESIUM
ION IN SOLUTION FOR THREE ADDED MAGNESIUM
ACETATE VALUES

Na₂SO₄ added in M/L × 10⁴	Residual Magnesium in Solution in M/L × 10⁴		
	36.0 × 10⁻⁴ M added	75.0 × 10⁻⁴ M added	150.0 × 10⁻⁴ M added
0.00	4.939	19.063	87.214
2.50	3.161	19.063	82.275
5.00	1.185	17.890	81.288
7.50	0.504	17.387	80.794
10.00	0.000ᵃ	17.087	80.596
15.00	0.346	16.445	80.498
25.00	0.049	17.384	80.201
50.00		16.988	79.806

ᵃ pH on this run was allowed to rise considerably above those of the others. Added aluminate = 18.0 × 10⁻⁴ M, pH adjusted to the average values of 8.6, 8.7, and 8.6 with either acetic or sodium hydroxide for the systems of added magnesium acetate 36.0, 75.0, and 150.0 × 10⁻⁴ M, respectively.
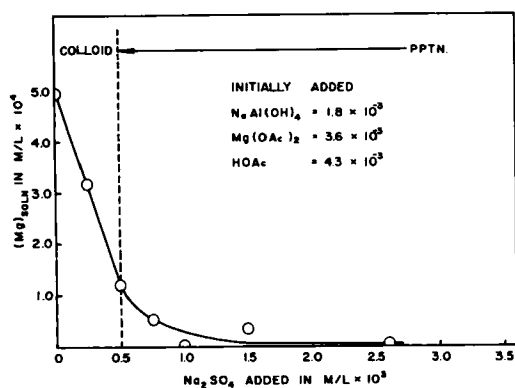

Fig. 9.—Changes in residual magnesium ion concentration exhibited by aluminate as a function of added sodium sulfate concentration in systems with an average pH value of 8.6.

added magnesium acetate of 3.60, 7.50, and 15.0 × 10⁻³ M, respectively.

With respect to the amount of magnesium bound in the precipitate, Fig. 10 shows that in the presence of excess sulfate ions the maximum atomic ratio of Mg:Al in the solid phase varied with added magnesium acetate as follows: magnesium acetate added in M/L × 10³, 3.60, 7.50, and 15.0, maximum Mg:Al atomic ratio in solid phase, 2.0, 3.3, and 3.9.

pH and Degree of Sulfate Binding.—The experimental values showing the effect of pH on the degree of sulfate binding as exhibited by 1.80 and 3.60 × 10⁻³ M of aluminate for various amounts of added magnesium acetate have been plotted in Figs. 11 and 12. The former covers the pH range of 7.5–10.0 and the latter from 9.0–14. The pH values were those elicited by the addition of appropriate amounts of acetic acid or sodium hydroxide.

Figure 11 indicates that pH had no apparent effect on the degree of sulfate binding in this range. The degree of sulfate binding seemed to approach a limiting value (ca. 0.8–0.9 × 10⁻³ M) when the added magnesium acetate concentration was equal to or greater than 4.0 × 10⁻³ M in a system that contained 1.80 × 10⁻³ M of aluminate. This corresponds roughly to Al:sulfate ratio of 2.0. Figure 12

shows essentially the same effect for pH values below 11.0 with the exception that the degree of sulfate binding had not reached a limiting value. At pH values greater than 11.0 the degree of sulfate binding decreased until no binding was exhibited at pH 12.5 or greater for a system containing 3.60 × 10⁻³ M of aluminate.

Effect of Sulfate Concentration on the Degree of Sulfate Binding.—The effect of increasing sulfate concentration on the amount of sulfate bound by the hydrous magnesium aluminate system is evident from Fig. 13. The apparent extent of sulfate binding appears to be essentially independent of the sulfate concentration when even a slight excess of the divalent ion was present. The amount of binding appears to correspond to slightly less than that expected on the basis of Al:sulfate ratio of two, particularly at low initial aluminate concentration.

The open circles in Fig. 13 represent systems containing 1.80 × 10⁻³ M aluminate and added magnesium acetate equal to or greater than 5.0 × 10⁻³ M. The half circles represent systems containing 3.60 × 10⁻³ M aluminate and added magnesium acetate equal to or greater than 8.0 × 10⁻³ M. The solid circles represent systems containing 5.10 × 10⁻³ M aluminate and added magnesium acetate (or magnesium sulfate) equal to or greater than 12.0 × 10⁻³ M. The technique described in the experimental procedure for phase solubility studies on buffered systems was utilized in this series of experiments. The exceptions were that the sulfate (added either as sodium or magnesium salt) concentration was the variable and that
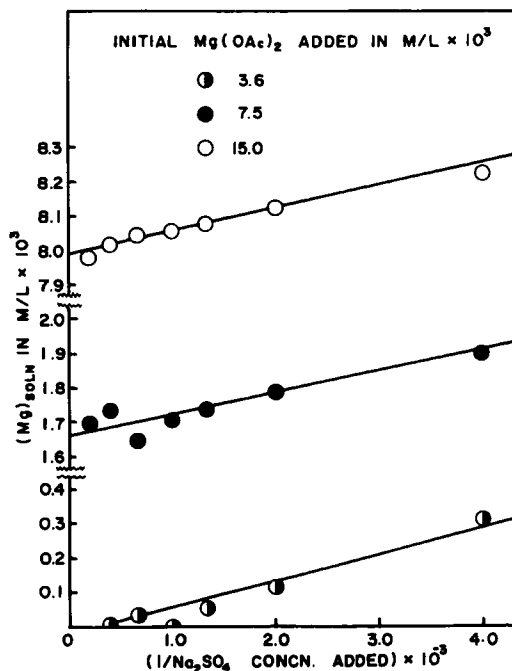

Fig. 10.—Changes in residual magnesium ion concentration exhibited by 1.80 × 10⁻³ M aluminate as a reciprocal function of added sulfate concentration for three values of added magnesium acetate in systems with average pH values of 8.6–8.7.
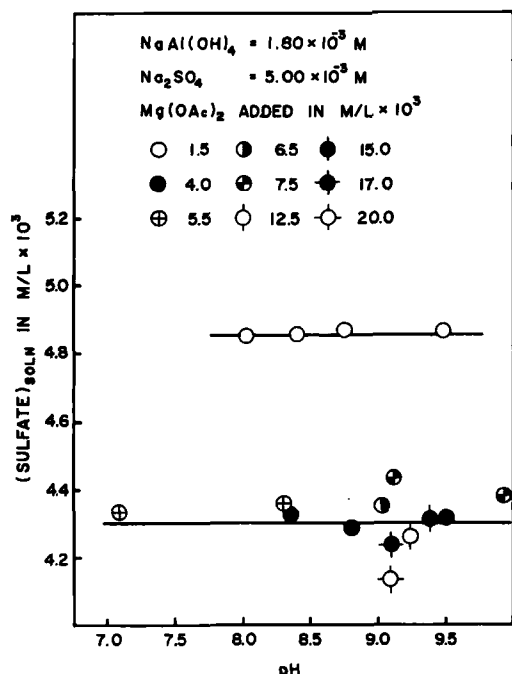
Fig. 11.—The effect of pH on the residual sulfate concentration in solution in systems containing aluminate and different values of magnesium acetate.
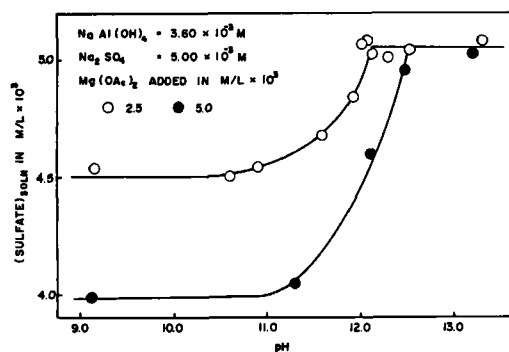

Fig. 12.—The effect of pH on the residual sulfate concentration in solution in systems containing aluminate and different values of magnesium acetate.

the system contained an excess amount of magnesium ions. At the end of the specified duration and conditions of equilibration, a 50-ml. aliquot sample of the filtered supernatant liquid was analyzed for the residual sulfate concentration according to the gravimetric method given earlier.

A study of Fig. 13 shows that the slopes of the three straight lines are all essentially in unity, indicating that further addition of sodium sulfate to the system caused only a corresponding increase in solution concentration. Under these experimental conditions the intercepts obtained by extrapolation of the linear portion of each curve provided the necessary composition information for the case of sulfate binding in the presence of excess of magnesium ions in solution. The results, when expressed as the atomic Al:sulfate ratios, are 2.5, 2.1,

and 1.9, respectively, for the given aluminate concentrations.

Effect of Magnesium Concentration on the Degree of Sulfate Binding.—Figure 14 shows the extent of binding of sulfate ions as a function of the added magnesium acetate concentration by systems containing 1.80, 2.55, 3.60, 5.10 $\times$ 10^{-3} M of aluminate, and 0–20.0 $\times$ 10^{-3} M of added magnesium acetate. These results are shown plotted for three initial concentrations of added sodium sulfate (2.5, 5.0, and 10.0 $\times$ 10^{-3} M).

Even a cursory examination of Fig. 14 reveals that all the curves appear to have several manifestations in common, chiefly in the form of linear dependency portions sandwiched between initial and final invariant plateaus relating the effects of added magnesium acetate concentration on sulfate binding.

The addition of small amounts of magnesium ions apparently did not produce sulfate binding. This region probably corresponds to the initial rise in magnesium concentration in solution as shown in Fig. 7. As more magnesium acetate was added, the sulfate ions reacted in the stoichiometric ratio of 4 Mg:1 sulfate, the linear dependency finally leveling off into an invariant plateau. This strongly suggests
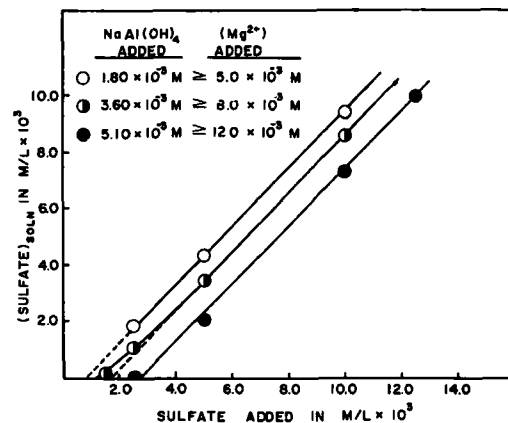

Fig. 13.—A phase solubility diagram showing the extent of sulfate binding exhibited by three concentrations of aluminate in the presence of excess of magnesium ions.
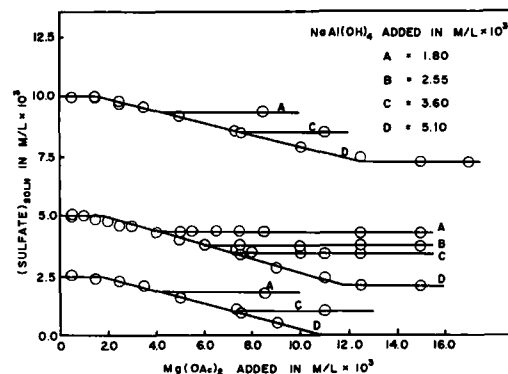

Fig. 14.—Changes in residual sulfate concentration in solution exhibited by several values of aluminate as a function of added magnesium acetate concentration for three added sodium sulfate concentrations.

that after the breakpoint sulfate was not being bound upon further addition of magnesium acetate. Figure 14 shows that these breakpoints depended mainly on the initially added sodium aluminate concentration. The stoichiometry at this point was approximately $4MgO \cdot Al_2O_3 \cdot SO_3 \cdot yH_2O$.

It should be kept in mind, however, that as indicated in Fig. 8, additional magnesium was taken up beyond the breakpoint. Eventually the final stoichiometry, as obtained in the presence of the large excess of magnesium ions indicated in a previous section, corresponds to $8MgO \cdot Al_2O_3 \cdot SO_3 \cdot zH_2O$. Since the Al:sulfate ratio is the same for both forms, Fig. 14 does not show further change in sulfate uptake beyond the breakpoint.

Phase Solubility Studies on Buffered Systems

The results reported in the preceding sections were obtained on systems initially containing only aluminate, acetate, sodium, magnesium, and sulfate ions, other than those contributed by water. Studies were also carried out with the addition of ammonium and chloride ions and ammonia particularly, since their presence permitted closer control of the relative basicity of the aqueous solutions. The behavior of the resulting and similar systems are substantially different from those of the unbuffered mixture and are reported in detail in this section.

Magnesium Binding and Effect of Buffer.— Figures 15 and 16 show the extent of magnesium ion binding exhibited by 1.80×10^{-3} M of aluminate containing 5.0×10^{-3} M sodium sulfate in presence of a relatively low buffer concentration of 1.0 $\times$
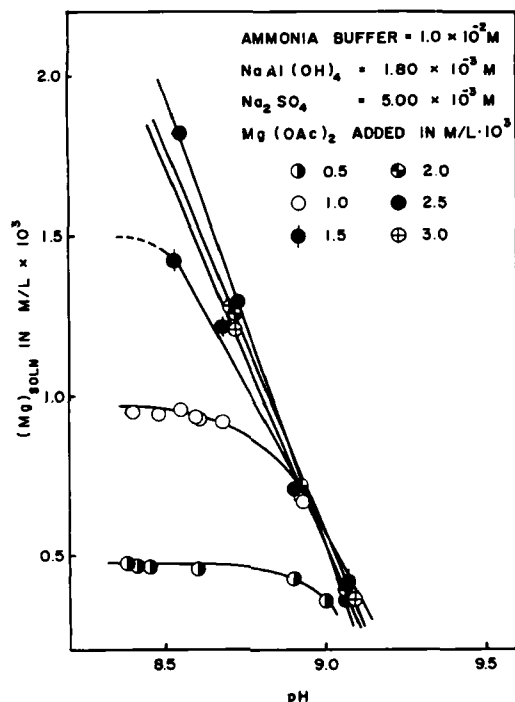

Fig. 15.—Changes in residual magnesium ion concentration in solution elicited by aluminate as a function of pH for several values of added magnesium acetate in buffered systems containing sulfate ions.

10^{-2} M ammonia buffer (adjusted with hydrochloric acid). Figure 15 covers the range of added magnesium acetate of $0.5–3.0 \times 10^{-3}$ M, and Fig. 16 from $3.5–8.5 \times 10^{-3}$ M. The pH values given were obtained by use of predetermined amounts of acetic acid or sodium hydroxide and the appropriate buffer. The data interpolated from the two plots were then used to construct Fig. 17. The four curves designated in Fig. 17 by open, half solid, and quarter circles represent systems with pH values of 8.50, 8.75, 9.00, and 9.25, respectively. These results were obtained by use of the bottle method as described in the experimental section. Predetermined volumes of solutions of the components were measured into each bottle in a definite order. The addition of buffer simply replaced part of the distilled water so that the final volume remained 100 ml. The aluminate solution used had a sodium hydroxide to aluminum hydroxide mole ratio of approximately 5.7. Other than the specified cases, these systems were equilibrated at 30° for five days or longer, after which the pH and the magnesium concentration in the supernatant liquid were determined.

The binding behaviors exhibited in the presence of 0.01 M ammonia buffer as shown in Fig. 17 differ largely from the unbuffered systems in the significantly higher magnesium concentrations required to form the insoluble species. The analysis of the straight line portions of the plots at high magnesium concentrations yield the relationships

System with pH	Slope of final portion of curve	Extrapolated Mg:Al atomic ratio
8.50	0.98	1.66
8.75	0.93	1.72
9.00	0.88	1.81
9.25	0.77	1.92

The influence of pH is obvious in that a change from 9.25 to 8.50 caused the slopes to approach unity and the extrapolated Mg:Al ratio to assume a lower value. The data shown above suggest that at higher pH values the system behaved much like the unbuffered, whereas at lower pH there is suggestive evidence of formation of another species corresponding possibly to an atomic ratio of three magnesium to two aluminum (or Mg:Al of 1.50). Similar results were also obtained with substantially higher (5×) buffer concentration, as shown in Fig. 18.

The data shown in Fig. 19 also suggest this type of relationship. The determinations in this instance were made with magnesium sulfate instead of the acetate, and variable amounts of the buffer were used. At lower buffer concentrations the results again resemble those from the unbuffered runs. At a higher buffer concentration, particularly with a shorter time of equilibration, the precipitated species correspond to three magnesium to two aluminum (7.6×10^{-3} M magnesium to 5.1×10^{-3} M aluminum). This suggests that the 3:2 species may be metastable relative to the 2:1 form.

Similar response to pH was exhibited when another buffer species was employed. Figure 20 shows the relation obtained when tris-(hydroxymethyl)-aminomethane (THMAM) was used as the buffering agent with two days of equilibration period. In Fig. 21 the corresponding plots of precipitated magnesium *vs.* the amount added in the form of magnesium sulfate is shown. At lower pH values it appears
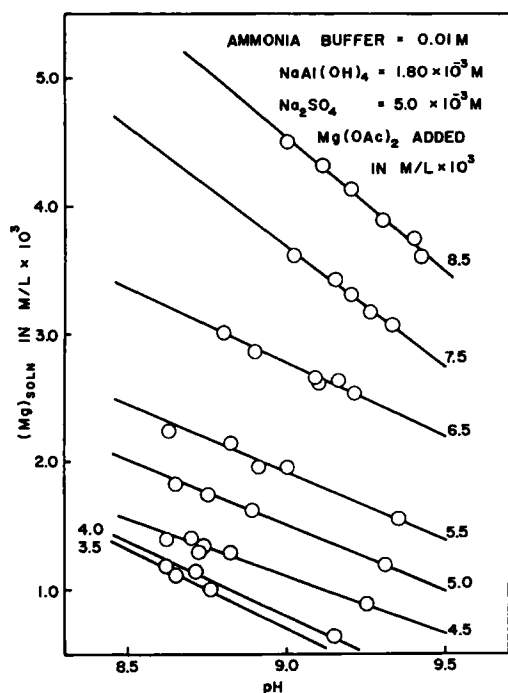
Fig. 16.—Changes in residual magnesium ion concentration in solution elicited by aluminate as a function of pH for several values of added magnesium acetate in buffered systems containing sulfate ions.
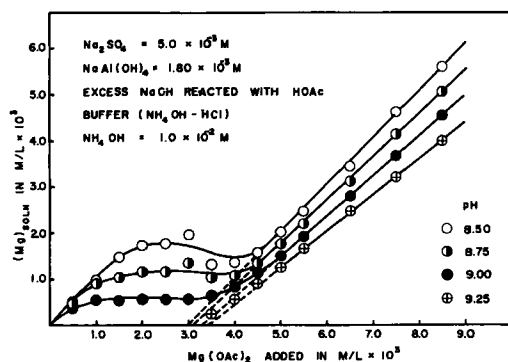

Fig. 17.—A phase solubility diagram showing the extent of magnesium ion binding exhibited by aluminate in buffered systems containing sulfate ions for four pH values.

that the break in the bound magnesium occurs at around 7.5×10^{-3} M corresponding again to 3:2 ratio. There appears to be another break at 1:2 ratio (2.5:5.1) which was not indicated in the ammonia systems. At higher pH there seems to be again the 2:1 relationship in presence of excess magnesium.

Sulfate Participation in the Buffered Systems.— It is evident from Figs. 19 and 20 that increasing the sulfate concentration reduces the amount of unbound magnesium ions in these systems. Thus, the species formed must again require sulfate ion in their formations. This is particularly evident in the data presented in Fig. 22, where the residual

concentration of magnesium has been plotted against the amount of sulfate added.

The influence of the buffer on the sulfate participation is also shown in Fig. 23, where the residual sulfate has been plotted as a function of added magnesium ions. The amount of bound sulfate (the difference between the added and the sulfate in solution) appears to be somewhat less (approximately 16 per cent) than that in the unbuffered system.

Since the formation of the solid species required sulfate, the effect of sulfate concentration in solution on the residual magnesium concentration in solution may be expected to follow the solubility product principle.

As shown in Fig. 24, a logarithmic plot of data given in Fig. 22 indicates that the sulfate concentration varied inversely as the third power of the magnesium ions. In the limit in presence of excess sulfate ions this also suggests that the solid species corresponds to the composition, 3 Mg:2 Al:1 sulfate for this system.

Properties of the Solid Species

X-Ray Diffraction Patterns.—Figure 25 shows the Debye-Scherrer patterns (25) of relative intensities of some of the stronger lines along with their angles of diffraction. The relative intensity was defined
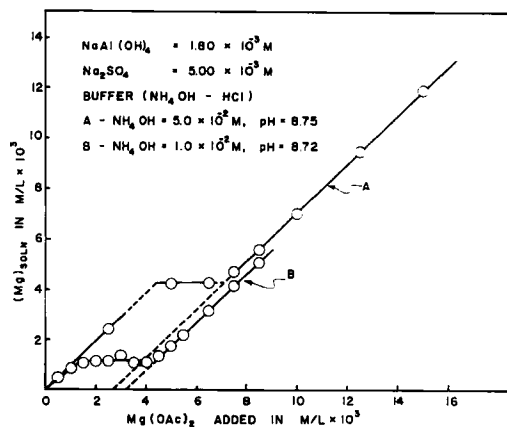

Fig. 18.—A phase solubility diagram showing the extent of magnesium binding exhibited by aluminate in presence of sulfate at two concentrations of ammonia buffer.
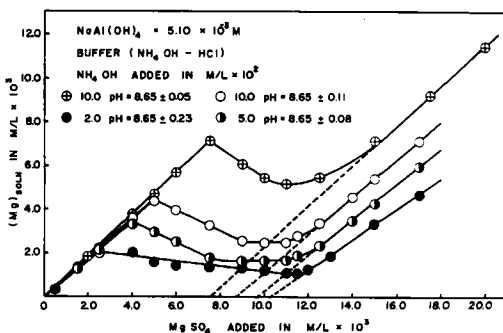

Fig. 19.—A phase solubility diagram showing the extent of magnesium binding exhibited by aluminate at various values of sulfate and three buffer concentrations, equilibration at five days ($\oplus$ = two days).
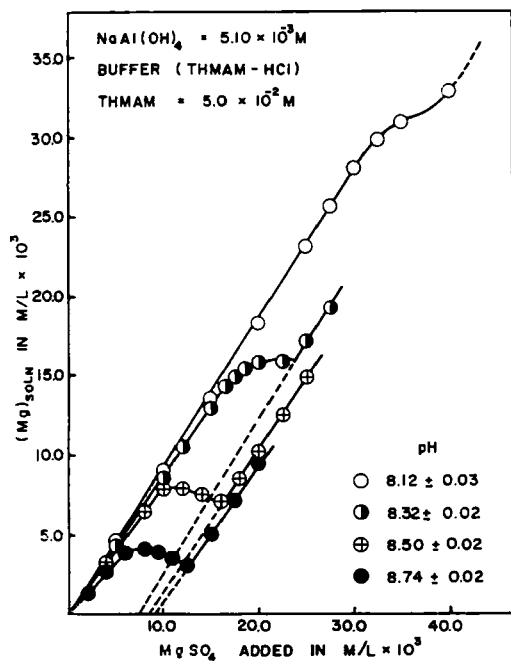
Fig. 20.—A phase solubility diagram showing the extent of magnesium binding exhibited by aluminate in buffered systems at various values of sulfate and pH with two days of equilibration.
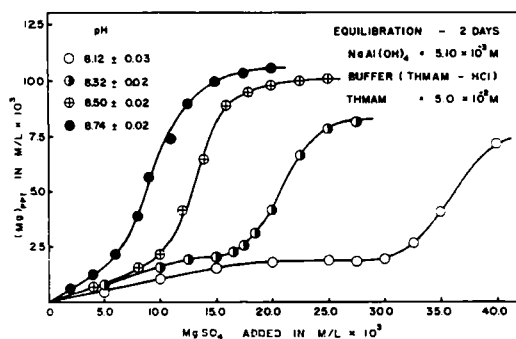

Fig. 21.—The amount of magnesium incorporated in the solid phase as a function of added magnesium sulfate concentration at four pH values in buffered systems containing aluminate with two days of equilibration.

as I/I_1, where I was the peak intensity of a diffraction line as estimated from per cent transmittance of the photographic negative corrected for background, and I_1 was the intensity of the strongest line of the particular phase in question. The diffraction patterns were developed by the use of filtered $CuK\alpha(\lambda = 1.5418 \text{ Å.})$ radiation on dried powdered samples (ground to about 200 mesh) with one hour exposure time on a camera film of 57.3 mm. in diameter. The relative information on the source and state of the powder samples is compiled in Table III. Samples A to E were isolated from phase solubility runs, washed with distilled water, and dried at room temperature and atmospheric pressure. Sample F was made batchwise, washed with distilled water, and dried over concentrated sulfuric acid at a reduced pressure for two weeks.

The effect of composition on the diffraction pattern as shown in Fig. 25 is of some interest. In particular the lines diffracted in the neighborhood of 30 and 33 degrees seemed to be shifted closer toward 30 degrees as the Mg:Al ratios increased. Another significant feature in these several patterns is the presence of an intense doublet at or close to the ten degree angle in samples A, B, and C, but which is either diffused or absent in the remaining samples.

All the samples indicated by the Debye-Scherrer patterns appeared at least partially crystalline and gave similar but significantly different X-ray diffraction patterns. For the series with Mg:Al ratios of 0.5 (A), 1.5 (B), 1.8 (C), and 4.0 (D), the line intensities as a whole increased as the ratios increased with the greatest distortion of lines in sample D (*cf.* Fig. 25).

Although the solid samples subjected to X-ray analysis were recovered directly from phase solubility runs, they were unfortunately subjected to varying degrees of washing with distilled water to remove the residual solution phase, as mentioned. This procedure probably produced significant alterations both in the crystal structures and the chemical compositions of the recovered dried products. Any serious attempts to derive structural information from the diffraction patterns should take this factor into account. The data presented in this section should, therefore, be considered as being indicative rather than conclusive, relative to the true structure of the precipitated species.
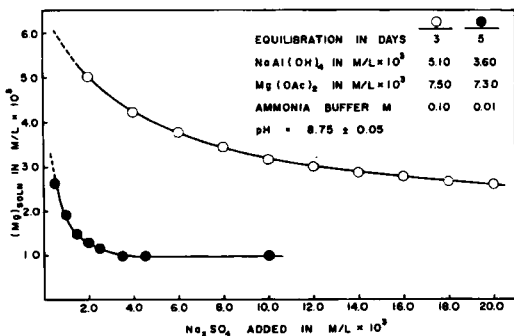

Fig. 22.—Changes in residual magnesium concentration in solution elicited by aluminate as a function of added sulfate concentration in buffered systems designated by open and solid circles.
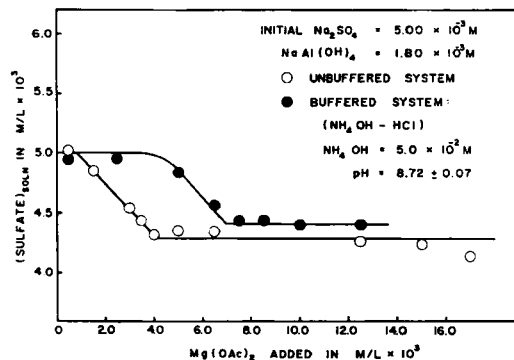

Fig. 23.—Changes in residual sulfate concentration in solution elicited by aluminate as a function of added magnesium acetate concentration in buffered and unbuffered systems.

CONCLUSION

The several solid species presumably formed in aqueous solutions by interactions of sodium, magnesium, aluminate, sulfate, and acetate ions in absence or presence of buffers are listed in Table IV. Their existence is proposed on the basis of experimental results presented in the preceding sections.

The evidence for the existence of species III and IV appears to be quite strong. The formation of species III which appears to be similar to the one reported by Hallmann (12) (who, however, indicated that sulfate was not part of the structure, but rather an impurity in the form of magnesium sulfate) is based on: (a) the phase solubility diagram obtained with the unbuffered sys-

Fig. 25.—Relative intensity and diffraction angle relation of some stronger lines from Debye-Scherrer patterns of several powder samples with various Mg:Al ratios (for source and state see Table III) developed with filtered $CuK\alpha$ radiation, one hour exposure, 57.3-mm. diameter camera.

tems (Fig. 7), (b) the potentiometric results given by magnesium acetate (Fig. 3), (c) the results from the sulfate study (Fig. 14), and (d) X-ray diffraction patterns (Fig. 25).

The phase solubility diagram shown in Fig. 7 gives extremely strong support to the existence of solid species III which apparently form in accordance with the phase rule (a solubility product-controlled process as evidenced by an invariant plateau). This certainly obviates the possibility of some of the earlier suggestions that solid solutions are possible over this range.

EQUILIBRATION · 3 DAYS

NaAl(OH)₄ · 5.10×10^{3} M

Mg(OAc)₂ · 7.50×10^{3} M
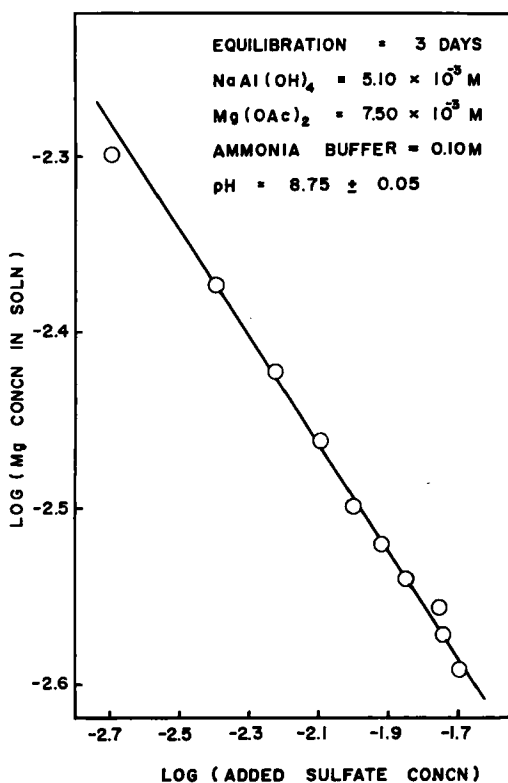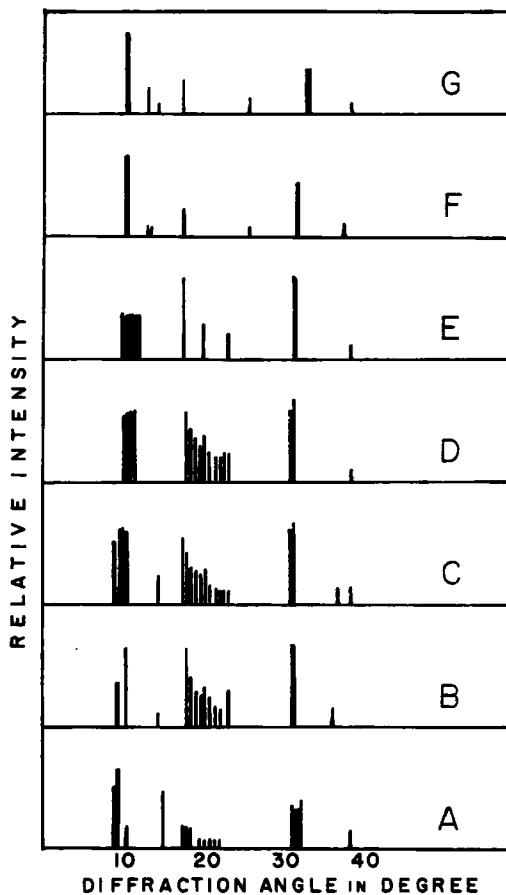
AMMONIA BUFFER · 0.10M

pH · 8.75 ± 0.05

Fig. 24.—Logarithmic relation of the concentrations of residual magnesium ion in solution and added sodium sulfate in buffered systems containing aluminate with three days of equilibration.

TABLE III.—INFORMATION RELATING TO THE SOURCE AND STATE OF THE X-RAY DIFFRACTION POWDER SAMPLES OBTAINED FROM PHASE SOLUBILITY STUDIES IN PRESENCE OF SULFATE

Sample	pH	Mg(OAc)₂ added in $M/L \times 10^3$	NaAl(OH)₄ added in $M/L \times 10^3$	Mg:Al ratio in ppt.
A	8.51	2.5	5.1	0.5
B	8.90	7.5	5.1	1.5
C	7.82	10.0	5.1	1.8
D	8.70	15.0	1.8	4.0
E[a]	8.72	12.5	1.8	1.7
F[b]	8.50	12.5	5.1	1.5

[a] Ammonia buffer = $1.0 \times 10^{-2} M$. [b] Ammonia buffer = $10.0 \times 10^{-2} M$.

TABLE IV.—SOLID SPECIES FORMED IN AQUEOUS SOLUTION BY INTERACTIONS OF SODIUM, MAGNESIUM, ALUMINATE, SULFATE, AND ACETATE IONS IN THE ABSENCE OR PRESENCE OF BUFFERS

Species	Composition	Conditions	Degree of Assurance
I	$MgO \cdot Al_2O_3 \cdot SO_3(?) \cdot nH_2O$	Low pH and high buffer concentration	Uncertain
II	$3MgO \cdot Al_2O_3 \cdot SO_3 \cdot xH_2O$	Low pH and moderate buffer concn.	Fair
III	$4MgO \cdot Al_2O_3 \cdot SO_3 \cdot yH_2O$	Unbuffered or at low buffer concn.	Definite
IV	$8MgO \cdot Al_2O_3 \cdot SO_3 \cdot zH_2O$	Unbuffered in an excess of Mg ion in solution	Definite

The 2 Mg:Al ratio of solid species III was obtained by the extrapolation of the rising portion of the curve to zero residual magnesium concentration in solution.

The composition of species III is also supported by the number of equivalents of hydrogen ion released when magnesium ion became bound through oxide to the aluminum system. Figure 3 shows that the amount of acetic acid required to obtain a pH value of approximately 8.5 in a system containing 1.80×10^{-3} M aluminate and excess sulfate is progressively decreased by addition of magnesium ions. The initial intensity of magnesium ionic binding appears to persist up to approximately two molar equivalents of aluminum present. The resulting composition corresponds to an atomic Mg:Al ratio of two to one, or that of solid species III.

Further evidence in support of the existence of species III is provided by the study of the effect of magnesium concentration on the extent of sulfate binding. The breaks in the plots shown in Fig. 14 indicate formation of a solid phase with an approximate 4 Mg:2 Al:1 SO₄ ratio which corresponds to that of species III.

Similar evidence is available in support of the existence of species IV. The phase solubility diagram as given in Fig. 8 provides the strongest indication for the formation of a solid species with the composition corresponding to that of species IV. This solid phase appears to form, however, without the characteristic invariant plateau. This behavior may be rationalized on the basis of a mass-controlled process rather than that of a solubility product. This is not an exception to the phase rule, but a modification with the addition of the mass law to account for the presumed dissociation phenomenon.

Figure 3 gives further support to the existence of solid species IV. The 4 Mg:1 Al ratio is obtained from the number of equivalents of hydrogen ion released when magnesium ions became bound through oxide to the aluminum system and by taking into account the effect of sulfate. The magnesium binding persists until approximately 12.6×10^{-3} mole per liter of hydrogen ions are released from 1.80×10^{-3} M aluminate. Since the sulfate effect is equivalent to 1.80×10^{-3}

moles per liter of hydrogen ions, the atomic Mg:Al ratio is approximately equal to $(12.6 + 1.8) \div (1.8 \times 2) \doteq 4:1$.

Supplementary evidence in the support of the existence of solid species IV is afforded by the X-ray patterns shown in Fig. 25 for the sample D with a 4 Mg:1 Al ratio which corresponds to that of the composition of species IV. The diffraction lines show the solid sample to be crystalline.

It is to be noted that species IV may be similar to one of the double hydroxides of magnesium and aluminum reported by Feitknecht, *et. al* (13–15). These double hydroxides differ from the present reported species by having a characteristic varying formula in which the sum of the number of atoms of magnesium and aluminum is equal to five, and which may also contain an atom of chlorine.

The evidence in support of the existence of species II is based on: (*a*) phase solubility diagrams obtained with buffered systems (Figs. 17, 18, and 19), (*b*) the results of magnesium and sulfate relation study in the reference system (Fig. 24) and (*c*) X-ray diffraction patterns (Fig. 25). The formation of species II is suggested by the phase solubility diagrams with buffered systems shown in Figs. 17, 18, and 19. The formation of the 3 Mg:2 Al solid species apparently require a combination of low pH value and moderate buffer concentration. The behavior of the system suggests, however, that solid species II may be metastable relative to species III, since a longer period of equilibration, higher pH values, or lower buffer concentration led to the formation of the latter solid phase.

The solubility product relationship as shown in Fig. 24 also indicates the presence of a 3 Mg:1 SO₄ species in this system. Since the system shows 3 Mg:2 Al ratio, the formation of a solid species may be rationalized to have the overall 3Mg:2 Al:1 SO₄ ratio, which corresponds to that of species II.

The Debye-Scherrer pattern of sample F with the Mg:Al ratio of 1.5 corresponding to the composition of the species II indicates that the species in question is at least partially crystalline. The unbuffered sample B and the buffered sample F are similar in composition; the difference in their

X-ray patterns may be due to drying conditions and to the effect of buffer in sample F.

Here again, species II may be similar to one of the double hydroxides reported by Feitknecht, since the number of atoms of magnesium and aluminum in species II does add up to five. However, species II has a sulfate moiety in the formula which the double hydroxides apparently lack.

The evidence citable in support of the existence of species I is based on (*a*) the phase solubility diagram shown in Fig. 20 and (*b*) the X-ray diffraction pattern in Fig. 25. The results of the data shown in the reference diagram indicate that species I required a combination of high hydrogen ion, high buffer, and low residual magnesium ion concentrations. These prerequisites are met in the system as designated by half and open circles in Figs. 20 and 21. Figure 21 shows clearly the presence of an invariant plateau in each of the systems with pH values of 8.12 and 8.32. These two curves indicate approximate atomic Mg:Al ratios of 1:2, which correspond to that of the solid species I.

It should be explicitly pointed out that in these studies no serious attempt was made to determine the extent of participation of singly charged ions other than H^+ and OH^-. Acetate, chloride, sodium, and other ions present probably were coprecipitated to varying degrees. It appears likely, however, that their presence does not seriously alter the qualitative nature of these findings.

The results of the present investigation, nevertheless, appear to show that the hydrous-sulfated magnesium aluminate system could very well exist in a number of solid species with different stoichiometric ratios. They also serve to illustrate the value of phase solubility studies in delineating complex inorganic systems.

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Triterpene Constituents of *Sarcostemma viminale* R.Br.

By JOHN D. TORRANCE and JOHANNES L. C. MARÁIS

The isolation of three triterpenes from a benzene extract of *Sarcostemma viminale* by alumina chromatography is described. Two of the triterpenes were identified as β-amyrin and friedelin, but the third, which occurred in the plant as an acetate, could not be identified with any known triterpene acetate. The monohydroxy-triterpene obtained by hydrolysis of the acetate has been designated viminalol.

S ARCOSTEMMA VIMINALE is a leafless, glabrous, fleshy climbing plant belonging to the natural order *Asclepiadaceae*. The plant, which has

numerous round-jointed stems and a slightly bitter milky latex, is found throughout Central and Southern Africa (1, 2) where it has been used medicinally by various tribes, both as an emetic and as a galactogogue ·(3). Steyn (4) found *Sarcostemma viminale* to be poisonous, and the plant is thought to be responsible for stock losses in southwest Africa (5).