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The influence of organic anions on the replacement of fixed phosphates at various pH levels.

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THE INFLUENCE OF ORGANIC ANIONS ON THE
REPLACEMENT OF FIXED PHOSPHATES
AT VARIOUS pH LEVELS

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THE INFLUENCE OF ORGANIC ANIONS ON THE
REPLACEMENT OF FIXED PHOSPHATES
AT VARIOUS pH LEVELS

by

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Thesis submitted for degree of
Master of Science

Department of Agronomy

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INTRODUCTION

Phosphorus has been called the master key to agriculture. A lack of phosphorus limits crop yields more frequently than does the lack of any other plant nutrient element. The recognition of this fact has resulted in an ever increasing demand for phosphatic fertilizers. In an attempt to meet this demand, the number of plants producing superphosphate in the United States increased more than 20 per cent in the six year period 1942 to 1948. Superphosphate production in 1948 rose 6 per cent above that of 1947, an increase of nearly 700,000 tons, but still the demand is greater than the supply. Most agricultural soils already contain large amounts of phosphate in relation to the quantity required for proper plant nutrition. It has been estimated that some soils which are considered as having an unusually low total phosphate content in reality contain a quantity sufficient to produce about 40 sixty-bushel crops of corn. In spite of this, the amount of soil-phosphate available to plants often is so small as to limit crop production. The application of phosphatic fertilizers to such soils does not always alleviate this condition; the crop is able to obtain in many instances less than 20 per cent of the phosphate applied. The necessity for the production of such large quantities of fertilizer phosphates is the direct result of the inefficient

recovery by the crops of the phosphate applied to soils. If it were possible to tap the relatively large reserve in the soil, or at least to prevent the fixation of applied phosphates, the quantity of phosphatic fertilizers required could be reduced to the level of that removed from the soil by cropping and erosion, with the resultant social and economic advantages of greater crop yields at lower production costs.

It is believed that iron and aluminum are chiefly responsible for the fixation of phosphate in acid soils. The manner in which the sesquioxides are translocated to the B horizon of podzol soils may provide a clue to the solution of the problem of phosphate fixation. The ability to form soluble complexes with iron and aluminum is well established as a property of certain of the better known organic acids (e.g. citric, tartaric, and oxalic acids). These and other organic acids represent a relatively large proportion of the products of microbial decomposition of organic residues, and in the genesis of podzol soils the soluble complexes formed with such acids are believed to be responsible to a great extent for the movement of iron and aluminum to the zone of illuviation. Thus it would appear that these organic anions under natural soil conditions were successful in competing with other anions - including phosphates - for those metals. This would suggest that actively decomposing organic matter in a soil might

provide an effective means for the prevention of phosphorus fixation.

Recent work at the University of Massachusetts lends support to such a view. Using pure solutions, iron and aluminum were each shown to combine with phosphate to produce a precipitate having an isoelectric pH of 3 to 4. Certain organic anions were shown to replace phosphate from these compounds to a marked degree at this pH range. Since these findings may lead eventually to the solution, or at least to an amelioration of the problem of phosphate fixation by soils, it is believed that this approach is of sufficient significance to warrant further investigation.

The purpose of this study was to determine by the use of pure solutions the extent to which certain organic anions would replace phosphorus fixed by iron and aluminum, and to learn their efficiency in this role at agricultural pH levels. In the course of the study, the phosphate-replacing ability of anions not previously dealt with was determined. A series of mono-, di-, and tricarboxylic acids having various combinations of amino and hydroxyl groups was used in an attempt to learn the characteristics of anions which influence their efficiency in preventing the fixation of phosphorus by iron and aluminum. Information was thus obtained regarding phosphate fixation and replacement which would be difficult to obtain or interpret if the more complex system involving soils and organic matter were used.

SCOPE OF THE PROBLEM OF PHOSPHATE FIXATION

Causes of Phosphate Fixation

It has long been observed that the soils on which crop production is limited because of the lack of phosphorus are those with exceptionally high iron and aluminum content. The red soils of the South are known to have a phosphate requirement of the highest order among the soils in the United States. The accumulation of phosphorus in the "iron crust" at the surface of laterites where it is deposited upon the rapid decomposition of plant residues has been reported by Joffe (16, p. 379)¹. Upon examination of podzol soils, it is to be noted that phosphorus is present principally in two regions of the profile: in the A₀ horizon in organic form, and in the B horizon where the highest concentration of the sesquioxides is also found. It has been well established that the major cause of phosphate fixation in acid soils is their free iron and aluminum content (2, 5, 18, 26, 28). Hall and Vogel (13) have pointed out that the reversion of phosphorus is dependent on the total active iron and aluminum in the soil, and not just that part which is soluble. Their absence or low content in a soil is accompanied by an increased mobility of phosphate. Thus Heck (15) reported that the penetration of phosphate applied

1. Figures in parenthesis refer to "Literature Cited", p. 30.

as topdressing was greatest in soils containing little active iron or aluminum. Neller (20) found that as much as 90 per cent of the soluble phosphorus added was leached from Florida's sandy soils.

It is believed by some investigators (22,7,19,1,6) that chemical reaction does not account entirely for the large amount of phosphorus held by a soil. The concept of phosphate adsorption on the extensive interfacial surface of soils is not without basis, and is generally accepted as contributing a share of phosphate fixation. That part of the adsorbed phosphate which is held at the micelle interface because of a difference in electrical charges is thought to be active in anion exchange, replaceable by other anions such as hydroxyl, fluoride, sulfate, and silicate.

The Effect of Soil Reaction on the Availability of Phosphate

In general it may be stated that fixation of phosphate in acid soils becomes greater as the acidity increases. Truog (31) states that phosphorus is most readily available in the pH range 6.5 to 7.5 since sufficient calcium is present to produce calcium phosphate, easily dissolved by the carbonic acid of the soil solution in that pH range. In support of this view, the application of lime has been shown by Parker and Tidmore (21) and other investigators to increase the availability of subsequently applied phosphates. The phosphate released in this manner, however, amounts to but a small per cent of the total fixed phosphate. Heck (15)

found that as the soil reaction dropped below pH 6.5, iron and aluminum reacted to a greater extent with phosphate due both to their increased activity and to the decrease in the amount of calcium which entered the fixation equilibrium. Two investigators (10,30) state that as the acidity becomes greater, phosphate fixation by iron continues to increase until a maximum is reached at a pH of 3.0. Romine and Metzger (23) have shown that low phosphate availability is correlated with low soil reaction. Working with the colloidal fractions of soils, both Roszman (24) and Coleman (6) found the pH range of maximum phosphate fixation to be between 3 and 4. In agreement, Swenson, Cole, and Sieling (29), using pure solutions, found the isoelectric point of iron phosphate to be in the region of pH 2.5 to 3.5, and that of the aluminum compound to be about 3.5 to 4.0. In his work with colloidal phosphate precipitates, Pugh (22) showed that as the pH is raised above the isoelectric point, hydroxyl ions will displace phosphate from the precipitate. This follows from a consideration of the fact that the isoelectric point of the hydroxide is at a much higher pH than that of the corresponding phosphate.

As the acidity is increased beyond the isoelectric point, iron and aluminum tend to go into solution with the simultaneous release of the fixed phosphate. As a result of this, the extraction of soils by dilute acids has been used by numerous investigators (23,11,4,17,28) in establish-

ing the fact that iron and aluminum are the principle causes of phosphate fixation in acid soils. In most instances the fixing capacity of the iron and aluminum in the acid extract was shown to be correlated with the fixing capacity of the soil before extraction, whereas the soil residue was found to retain little or no power to fix phosphate.

Effect of Organic Matter on the
Fixation of Phosphate

Organic matter is now generally believed to be important in promoting greater phosphate availability. Since the relatively more stable fraction of soil organic matter is known to have the greater influence on many soil properties, a number of investigators directed their attention toward the determination of its effect on phosphate fixation, with results ranging from reports of little or no effect to greatly increased phosphate availability. Doughty (11) found that peat was capable of fixing some phosphate, but concluded that synthetic and natural humus did not. On the other hand, Heck (14) observed that the availability of phosphate in lateritic soils varied proportionately with the organic matter content. Humus and lignin have recently been shown to be effective in replacing phosphate from basic iron and aluminum phosphates prepared from pure solutions (29).

Other investigations (8,1) have indicated that it is the actively decomposing organic matter which is most

effective in the prevention of phosphate fixation. Weir (32, page 267) points out that phosphorus may become extremely mobile in the presence of large amounts of actively decomposing organic matter with severe loss by leaching.

He states:

In Wisconsin, a study was made of the phosphorus losses on sixteen tobacco fields. These fields were cropped, on the average, forty-six years-- thirty of which were tobacco. During that time they received an average of thirty applications of manure at the rate of eighteen loads, or about twenty-seven tons, to the acre. These investigations showed that during the forty-six year cropping period, this system of farming caused the loss (above that removed by the crops) of an amount of phosphorus per acre from the surface soil eight inches deep, sufficient to supply the phosphorus needs of at least seventy 75-bushel corn crops.

Several theories have been advanced as to the processes by which organic matter increases the availability of phosphate. Metzger (18) and Scarseth (25) believe that the presence of organic matter and carbon dioxide produced on its decomposition reduces the amount of active iron or aluminum in the soil. Others (28,15) conclude that organic anions present as decomposition products have a greater chemical affinity for iron and aluminum than do the active phosphate ions. Buchanan (3, page 257) believes that microbiological activity in the soil is responsible for the conversion of certain insoluble compounds of phosphorus into available form. He further states that it is probable that the organisms do not directly attack the phosphates, but that the changes are brought about by the decomposition

products of organic matter in the soil. The reduction in phosphate fixation noted when superphosphate is mixed with manure before application to soil is thought to be a combination of effects: its ingestion, conversion to organic form and subsequent slow release by the active microbial population; the formation of less soluble products with the manure, reducing its contact with the soil; and the pelletting action caused by the wet manure. It is likely that each of these processes contributes its share in promoting phosphate availability.

EXPERIMENTAL

The two principal objectives sought in this study were: a) to establish a lyotropic series of organic anions according to their ability to prevent fixation of phosphate by iron and aluminum, and b) to determine the effect of pH on their replacing powers. Using pure solutions, iron and aluminum will react with phosphate to form an insoluble precipitate. At any given pH, the difference in the quantity of phosphate contained in such precipitates formed in the presence and in the absence of an organic anion was assumed to be a measure of the effect which the anion exerted on the system. It was believed that such an effect could best be shown under equimolar competition between the phosphate and the organic anions, and this basis was used for comparison throughout the course of the investigation. In order to determine the effect of pH, varying quantities of sodium hydroxide were added to each system. The data of Swenson, Cole, and Sieling (29) showed the isoelectric point of iron phosphate to be about pH 3, and that of aluminum to be about pH 4. On this basis, these values in each case were chosen as the lower limit of pH to be studied. Sodium chloride was added in a quantity sufficient to provide a one per cent concentration in the final volume in order to suppress the adsorption of phosphate by the precipitates formed and to prevent their peptization.

Preparation of Solutions

Davis (9) has shown that in the pH range of acid soils phosphorus is present in solution predominantly as the H_2PO_4^- ion. A solution of potassium di-hydrogen phosphate was therefore used to furnish this ion in the system studied. A 0.4 molar stock solution was prepared by dissolving 54.4520 g. of reagent quality KH_2PO_4 in distilled water sufficient to bring the final volume to one liter. This solution was standardized colorimetrically by the Sherman method (27). As it was needed, a 0.04 molar working solution containing five per cent sodium chloride was made by diluting 200 ml. of the stock solution and 100 g. of sodium chloride to two liters with distilled water. Twenty-five ml. of this working solution was used throughout the course of this study to provide one millimol of phosphorus and the desired concentration of sodium chloride.

A stock solution of ferric chloride was prepared by adding 110 ml. of concentrated hydrochloric acid to approximately 200 g. of ferric chloride and diluting to 2 liters. The solution was standardized by the 8-hydroxy-quinoline method. From this solution was prepared a 0.02 molar working solution, which was used as the source of iron in this investigation.

Aluminum ion was furnished by a 0.02 M aluminum chloride solution, prepared by dissolving 1.0788 g. of aluminum foil in 100 ml. of 1.324 normal hydrochloric acid and diluting to

2 liters.

Freshly prepared solutions of organic acids were used to provide the various organic anions as needed. Theoretical quantities as calculated from their molecular weights, were dissolved in sufficient distilled water to obtain the desired concentrations.

A carbonate free stock solution of 0.2 normal sodium hydroxide was prepared and used to adjust the pH of the various systems.

Method of Procedure

Establishment of Standard Values of Phosphate Fixation by

Iron and Aluminum at Various pH Values. The extent to

which phosphate will react with iron or aluminum at equimolar concentration was determined at various pH values by the following method:

A series of 250 ml. beakers was set up. Into each was pipetted 25 ml. of 0.04 M potassium acid phosphate, and 50 ml. of 0.02 M ferric chloride or aluminum chloride. Distilled water was added to the beakers in quantities sufficient to make a final volume of 125 ml. after the addition of sodium hydroxide. The solutions were brought to a boil, and successively increasing portions of 0.2 N sodium hydroxide were added to the beakers with vigorous stirring. The mixtures were kept at a slow boil for thirty minutes in order to hasten the establishment of equilibrium. They were then permitted to cool to room temperature, and the pH of

each was determined with a Beckman pH meter. They were again heated to boiling, and filtered while hot. The beakers and precipitates were washed with one per cent sodium chloride solution adjusted to the pH at which the precipitate was formed. Hot 1 per cent perchloric acid was used to dissolve the precipitates, and the phosphorus content of the resultant solutions were determined colorimetrically.

The values for the per cent of phosphate fixed by iron and aluminum at various pH levels are given in tables 1 and 2, and are shown graphically by the curves labeled "Blank" in figures 1 and 2.

Table 1

The influence of pH on the fixation of phosphorus by iron at equimolar concentrations

| <u>ml. NaOH</u> | <u>pH</u> | <u>% phosphorus fixed by iron</u> |
|-----------------|-----------|---------------------------------------|
| 15.0 | 3.01 | 90.2 |
| 16.3 | 4.19 | 88.3 |
| 17.1 | 5.23 | 86.3 |
| 17.9 | 5.98 | 82.5 |
| 19.3 | 6.93 | 77.5 |
| 21.5 | 7.98 | 60.2 |

Table 2

The influence of pH on the fixation of phosphorus by aluminum at equimolar concentrations

| <u>ml. NaOH.</u> | <u>pH</u> | <u>% phosphorus fixed by aluminum</u> |
|------------------|-----------|---|
| 12.7 | 4.09 | 86.1 |
| 13.3 | 5.13 | 85.1 |
| 14.1 | 6.03 | 83.5 |
| 15.5 | 7.03 | 79.7 |
| 16.6 | 7.90 | 75.5 |
| 18.1 | 9.00 | 67.1 |

The results showed that less phosphate is fixed by iron and aluminum as the acidity decreases. This was in agreement with the findings of numerous investigators (15,21,22,23,24,30) in their work with both pure solutions and with soils. It is to be noted that the reduction of phosphate fixation with an increase of pH was greater in the case of iron than with aluminum. The significance of this observation lies in the fact that the iron-fixed phosphate is rated by some investigators (12,15,18) as being more difficultly available to plants than is that fixed by aluminum. Therefore the correction of soil acidity would reduce the amount of phosphorus fixed in the soil in its least available form.

The Effect of Organic Anions on the Fixation of Phosphate at Various pH Levels. The laboratory procedure used to determine the influence of organic anions on phosphate fixation was essentially the same as that described for determining the effect of pH on phosphate fixation. The only difference in the procedures was that a solution containing one millimol of the organic anion was added to the phosphate solution in the beaker before adding the iron or aluminum solution. In this way both competing anions being studied were present when the iron or aluminum solution was introduced, and equilibrium could be established more readily.

The following acids were used to furnish the organic anions studied: dl α -alanine, dl aspartic, citric, dl lactic, dl malic, malonic, oxalic, succinic, and dl tartaric.

It was found to be impracticable to adjust the pH of the solutions at will to any definite desired value because of the complex nature of the systems involved. Instead, a number of random values were determined within the desired pH limits, and the results plotted as shown in figures 1-6. The phosphate fixation percentage at each pH value was then obtained from these curves.

Results

The data shown on tables 3 and 4 represent a summary of the results obtained in this study.

Table 3

Per cent of phosphate fixed by Iron at various pH levels as influenced by the presence of organic anions

| pH | 3 | 4 | 5 | 6 | 7 | 8 |
|----------------------------|------|------|------|------|------|------|
| Blank* | 90.2 | 88.8 | 86.4 | 83.0 | 76.9 | 59.0 |
| α -amino-propionate | 88.6 | 86.3 | 83.7 | 80.7 | 77.1 | 70.0 |
| Aspartate | 90.2 | 88.8 | 87.1 | 85.6 | 83.1 | 85.8 |
| Citrate | 36.5 | 10.0 | 5.4 | 16.1 | 33.5 | 29.8 |
| Lactate | 84.9 | 84.0 | 84.4 | 80.6 | 68.1 | 25.0 |
| Malate | 85.3 | 78.9 | 79.4 | 82.0 | 79.2 | 65.9 |
| Malonate | 84.1 | 82.0 | 80.8 | 79.1 | 70.3 | 40.0 |
| Oxalate | 47.8 | 51.9 | 53.3 | 59.0 | 56.9 | 42.3 |
| Succinate | 91.7 | 89.4 | 87.5 | 85.2 | 79.5 | 64.0 |
| Tartrate | 61.2 | 66.4 | 71.2 | 70.8 | 64.1 | 00.0 |

* No organic anion present.

Table 4

Per cent of phosphate fixed by Aluminum at various pH levels as influenced by the presence of organic anions

| pH | 4 | 5 | 6 | 7 | 8 | 9 |
|----------------------------|------|------|------|------|------|------|
| Blank* | 86.2 | 85.3 | 83.6 | 79.9 | 75.0 | 67.1 |
| α -amino-propionate | 86.2 | 85.3 | 83.8 | 81.2 | 77.7 | 71.3 |
| Aspartate | 84.8 | 83.7 | 81.7 | 78.1 | 73.1 | 62.0 |
| Citrate | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Lactate | 82.6 | 80.8 | 74.5 | 67.6 | 60.7 | 49.9 |
| Malate | 70.4 | 72.4 | 76.3 | 71.3 | 64.5 | 54.8 |
| Malonate | 59.2 | 66.2 | 71.8 | 70.3 | 62.9 | 54.5 |
| Oxalate | 42.8 | 48.8 | 62.5 | 70.0 | 66.8 | 60.4 |
| Succinate | 84.1 | 81.0 | 78.6 | 72.9 | 64.7 | 55.4 |
| Tartrate | 72.8 | 74.8 | 75.2 | 71.0 | 63.7 | 52.3 |
| .25 Citrate# | 60.6 | 59.3 | 57.6 | 55.9 | 54.2 | 52.5 |

* No organic anion present.

0.25 millimol citrate.

It is to be noted that the percentages shown are based upon the full millimol of phosphate originally present in the system. One millimol of organic anion and one millimol of iron were also present, and thus the results are based upon an equilibrium established between equi-molar concentrations of these ions. The equilibrium is seen to be influenced by the concentration of hydroxyl ion present, as indicated by the variation in the percents of phosphate fixed as the pH increases. Examining the data from another viewpoint, tables 5 and 6 were designed to show the percents of the fixed phosphorus which would become available to plants if the same reactions were caused to take place in soils of the given pH levels.

Table 5

Per cent of the iron-fixed phosphate replaced by organic anions at various pH levels

| pH | 3 | 4 | 5 | 6 | 7 | 8 |
|----------------------------|------|------|------|------|------|-------|
| α -amino-propionate | 1.4 | 2.8 | 3.1 | 2.8 | x | x |
| Aspartate | 0.0 | 0.0 | x | x | x | x |
| Citrate | 59.6 | 88.7 | 93.7 | 80.6 | 56.4 | 49.5 |
| Lactate | 5.9 | 5.4 | 2.3 | 2.9 | 11.4 | 57.6 |
| Malate | 5.3 | 11.1 | 10.6 | 1.2 | x | x |
| Malonate | 6.8 | 7.7 | 6.6 | 4.7 | 8.6 | 32.2 |
| Oxalate | 47.0 | 42.6 | 38.3 | 28.9 | 26.0 | 28.3 |
| Succinate | x | x | x | x | x | x |
| Tartrate | 32.2 | 25.2 | 17.6 | 14.7 | 16.6 | 100.0 |

x Phosphorus fixation was increased by the presence of the organic anion.

Table 6

Per cent of the aluminum-fixed phosphate replaced by organic anions at various pH levels

| pH | 4 | 5 | 6 | 7 | 8 | 9 |
|----------------------------|-------|-------|-------|-------|-------|-------|
| α -amino-propionate | 0.0 | 0.0 | x | x | x | x |
| Aspartate | 1.6 | 1.9 | 2.3 | 2.3 | 2.5 | 7.6 |
| Citrate | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| Lactate | 4.2 | 5.3 | 10.9 | 15.4 | 19.1 | 25.6 |
| Malate | 18.3 | 15.1 | 8.7 | 10.8 | 14.0 | 18.3 |
| Malonate | 31.3 | 22.4 | 14.1 | 12.0 | 16.1 | 18.8 |
| Oxalate | 50.3 | 42.8 | 25.2 | 12.4 | 10.9 | 10.0 |
| Succinate | 2.4 | 5.0 | 6.0 | 8.8 | 13.7 | 17.4 |
| Tartrate | 15.5 | 13.2 | 10.0 | 11.1 | 15.1 | 22.1 |
| .25 Citrate# | 29.7 | 30.5 | 71.1 | 30.0 | 27.7 | 21.8 |

x Phosphorus fixation was increased by the presence of the organic anion.

0.25 millimol citrate

The results become more obvious when shown graphically. Figures 1 and 2 represent a series that shows the effects which hydroxyl and amino groups in the compound had on their phosphate-replacing capacity. The acids acting as the source of the anions were respectively: succinic, aspartic (amino-succinic), malic (hydroxy-succinic), and tartaric (α, β dihydroxy-succinic) acids. A comparison of these curves reveals that the presence of hydroxyl groups increased the effectiveness of an organic anion in preventing the fixation of phosphate, whereas the presence of the amino group did not appreciably influence this property. The malate ion was most effective at a range between pH 4 and 5 in both the iron and aluminum systems. The effect of the tartrate ion on the prevention of phosphate fixation was greater with iron than with aluminum. In these figures

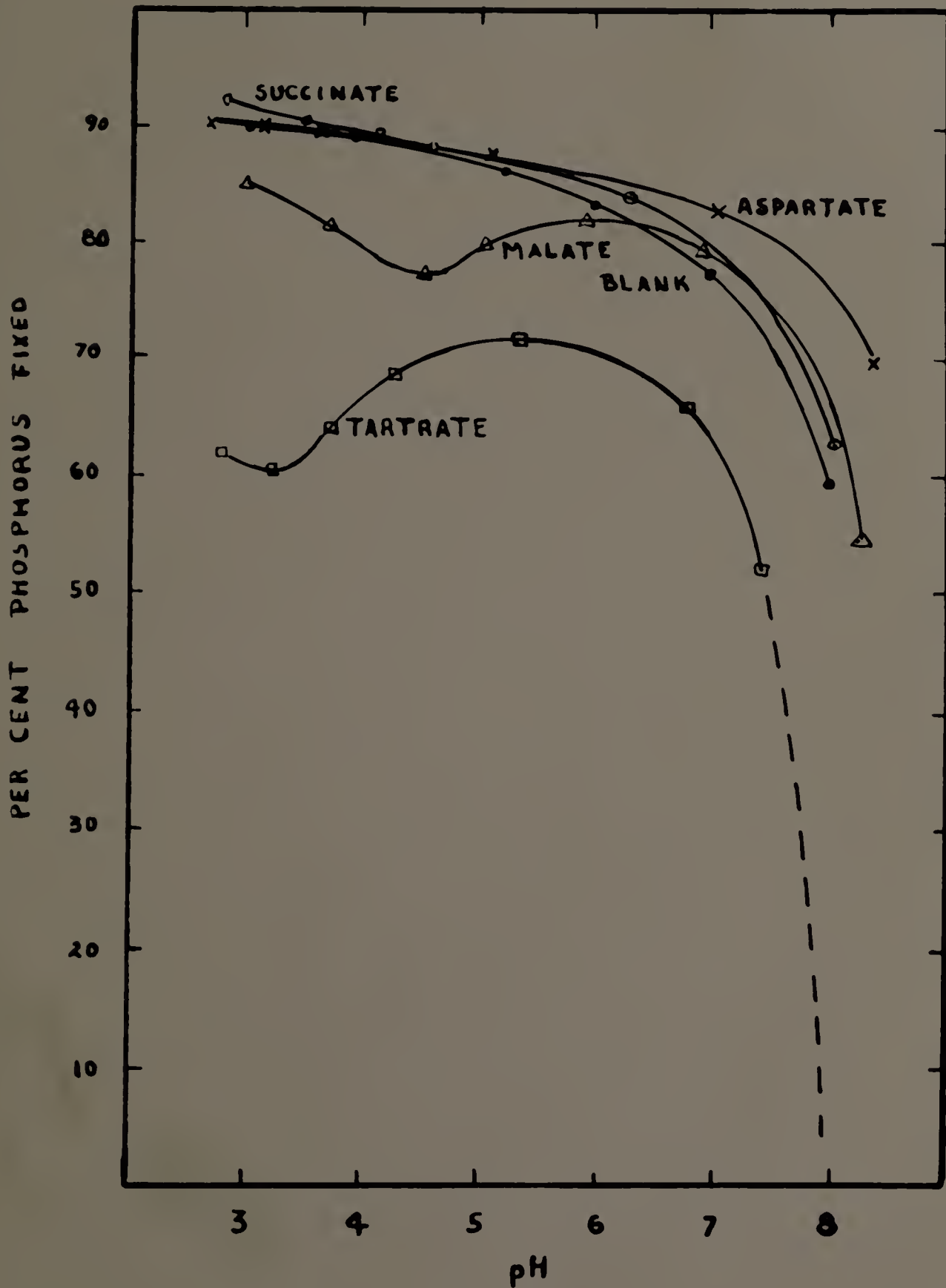


Figure 1. The influence of pH on the effectiveness of succinate, malate, tartrate, and aspartate ions in preventing phosphate fixation by iron.

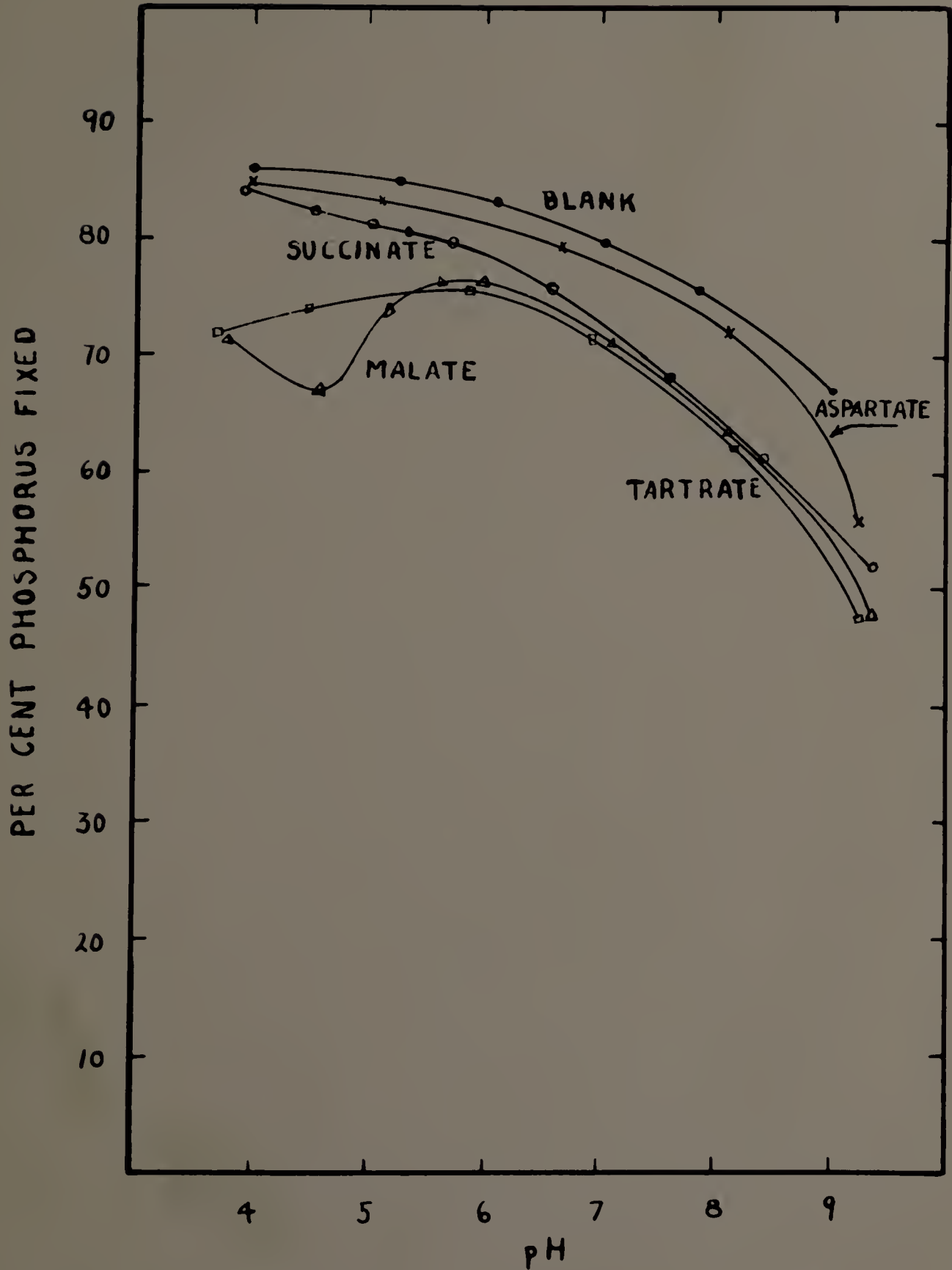


Figure 2. The influence of pH on the effectiveness of succinate, malate, tartrate, and aspartate ions in preventing phosphate fixation by aluminum.

as in those which follow, the curves labeled "Blank" represent the standard phosphate-fixing capacity of iron or aluminum as influenced by hydroxyl ion only, no organic anion being present.

Figures 3 and 4 are presented to show the effect which the increasing length of carbon-chain had on the efficiency of organic anions in preventing phosphate fixation. The oxalate, malonate, and succinate ions have a carbon-chain length of 2, 3, and 4 respectively; they are all dicarboxylic acids and have no hydroxyl- or amino-substituted groups. The succinate curves are observed for the second time in these figures in order to provide ease of comparison. This series disclosed that in acid solutions, the shorter-chain compound had the greater effect in reducing the fixation of phosphate by both iron and aluminum. The malonate ion apparently complexed with aluminum but not with iron. The influence of the succinate ion was not significant in either system, nor was it appreciably affected by changes of pH. The activity of the acid groups of the dicarboxylic acids are known to increase directly with their mutual proximity. This probably explains their apparent tendency to assume a reversed order at the upper pH limits studied, since the more active hydrogens of the oxalic acid, for instance, would be the first to be completely neutralized by an increase of hydroxyl ions, thus leaving it without influence on the system.

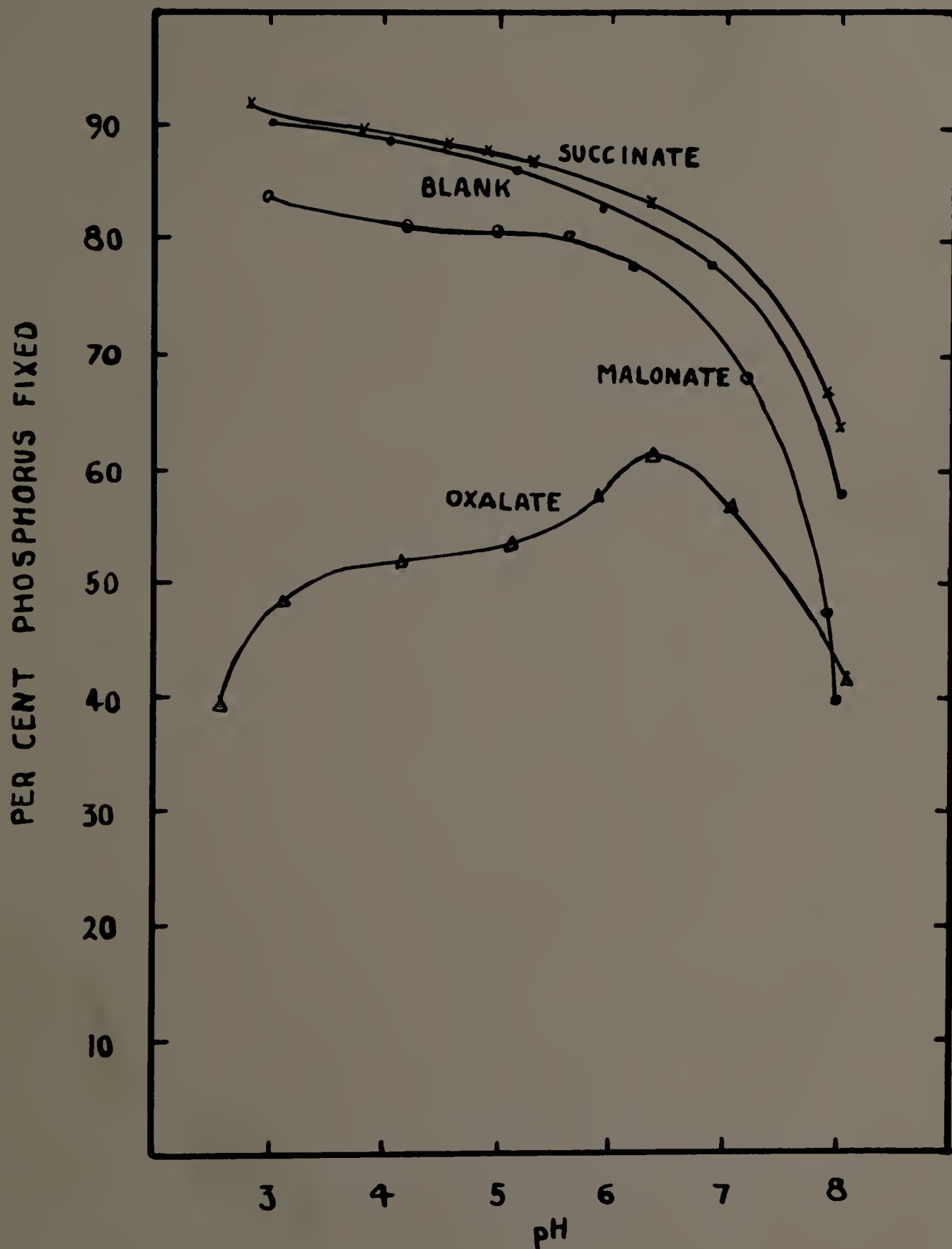


Figure 3. The influence of pH on the effectiveness of succinate, malonate, and oxalate ions in preventing phosphate fixation by iron.

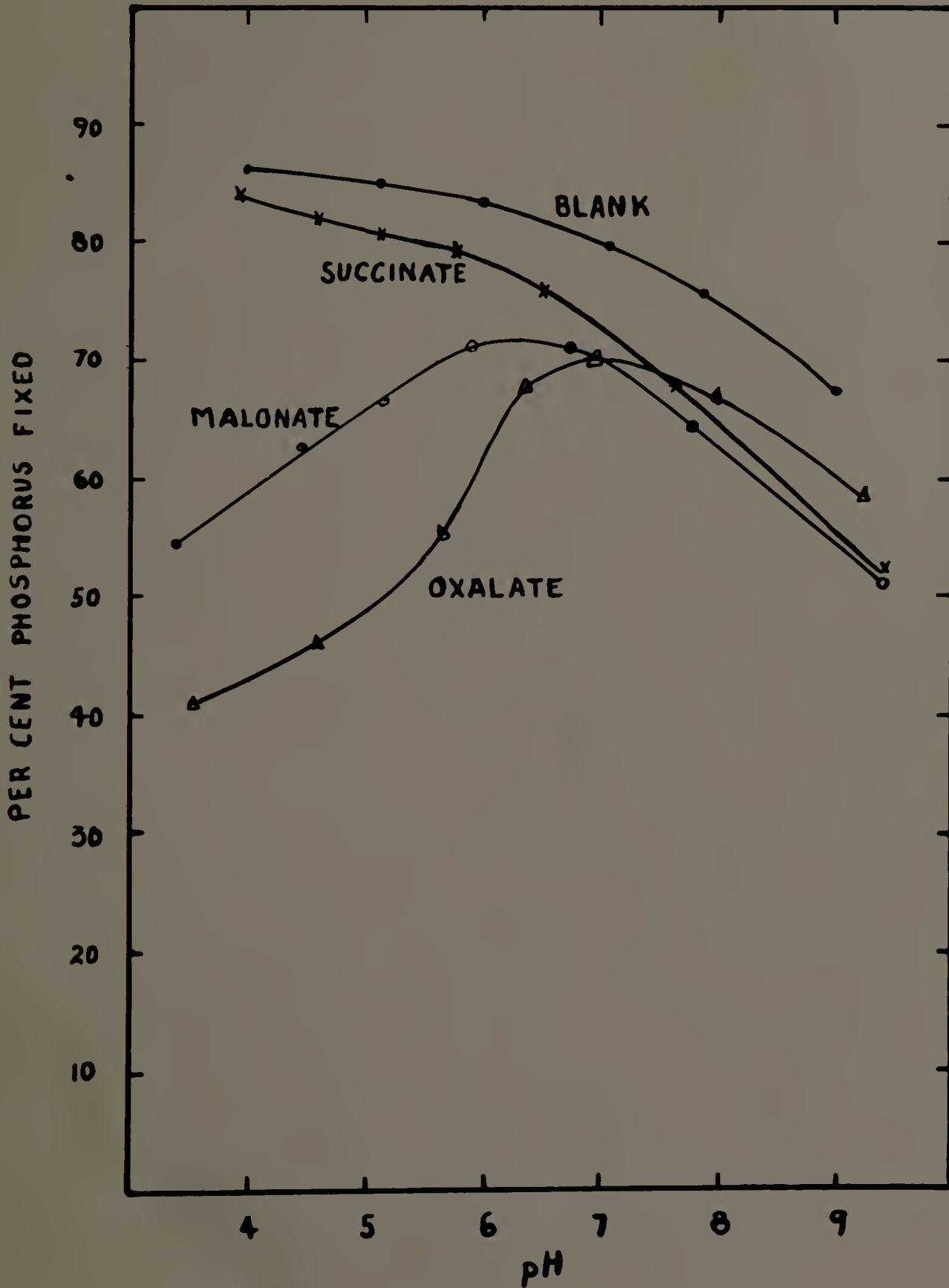


Figure 4. The influence of pH on the effectiveness of succinate, malonate, and oxalate ions in preventing phosphate fixation by aluminum.

The curves as influenced by the anions of citric, malic, lactic acids and alanine (amino-propionic acid), shown in figures 5 and 6, provide an interesting study. Comparing the curves established in the presence of lactic and malic acids, it is seen that at the higher pH levels, lactic was the more effective. Malic acid has two carboxyl groups as opposed to lactic acid's one, but the added length of the former's carbon-chain apparently counterbalances this advantage. The curves of phosphate fixation showing the effects of alanine and lactic acids are of interest. They are similar compounds except that alanine contains an amino group and lactic acid contains an hydroxyl group. The amino acid had little effect in preventing phosphate fixation, but the lactic acid was quite effective at the higher pH values. These results are similar to those found by comparing malic and aspartic acids.

Citric acid appears to be in a class by itself. The hydroxyl and carboxyl groups attached to the central carbon of this relatively large molecule cause both to be more active chemically. It should be pointed out that the curve shown for the effect of citric acid in figure 6 is in reality the effect of but 0.25 millimol of citric acid in the presence of one millimol each of aluminum and phosphorus. As little as half a millimol of citrate was found to be effective in completely preventing phosphate fixation by aluminum. When 0.4 millimol of citrate was used, a slight

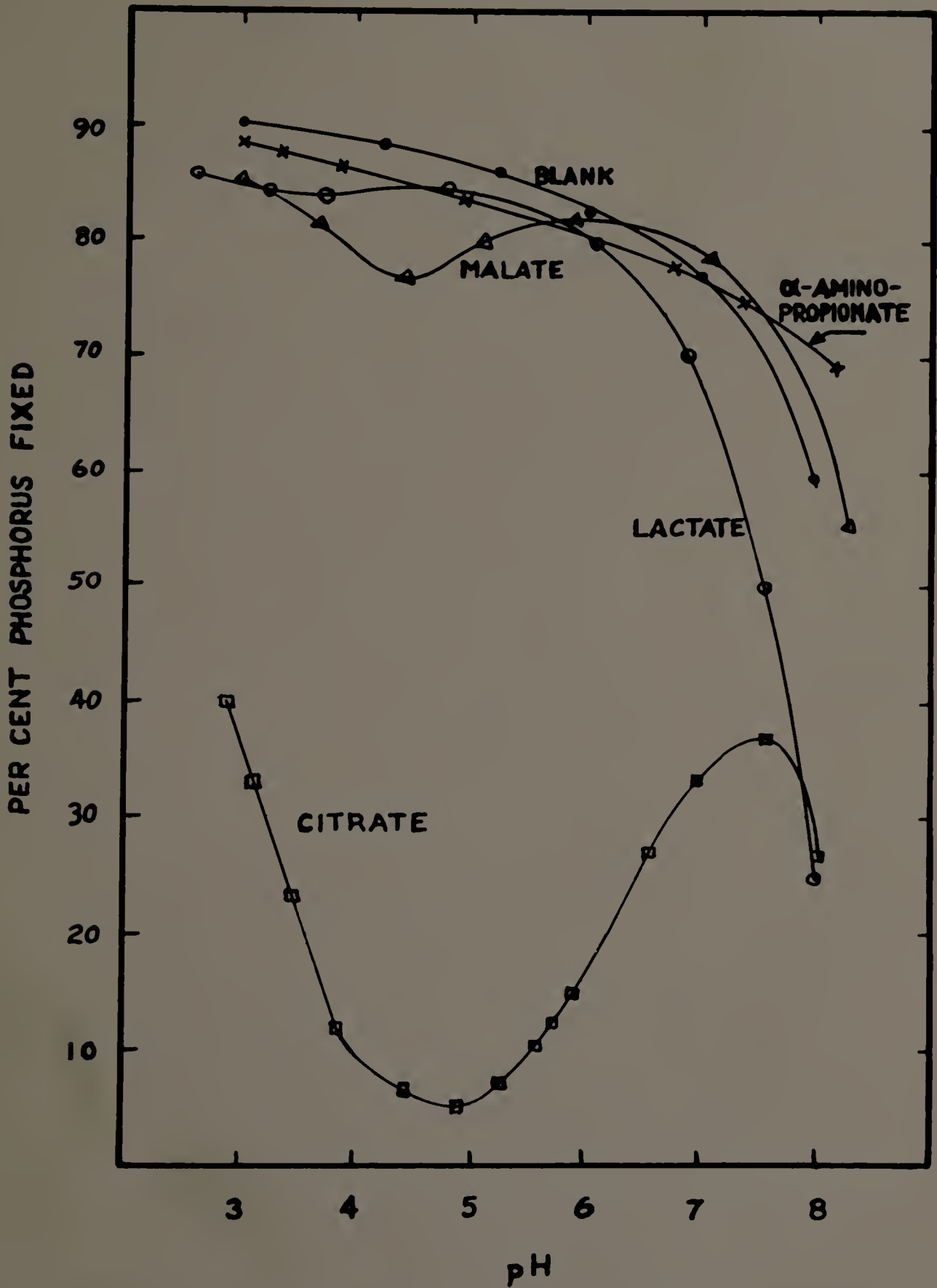


Figure 5. Influence of pH on the effectiveness of lactate, malate, α -aminopropionate, and citrate ions in preventing phosphate fixation by iron.

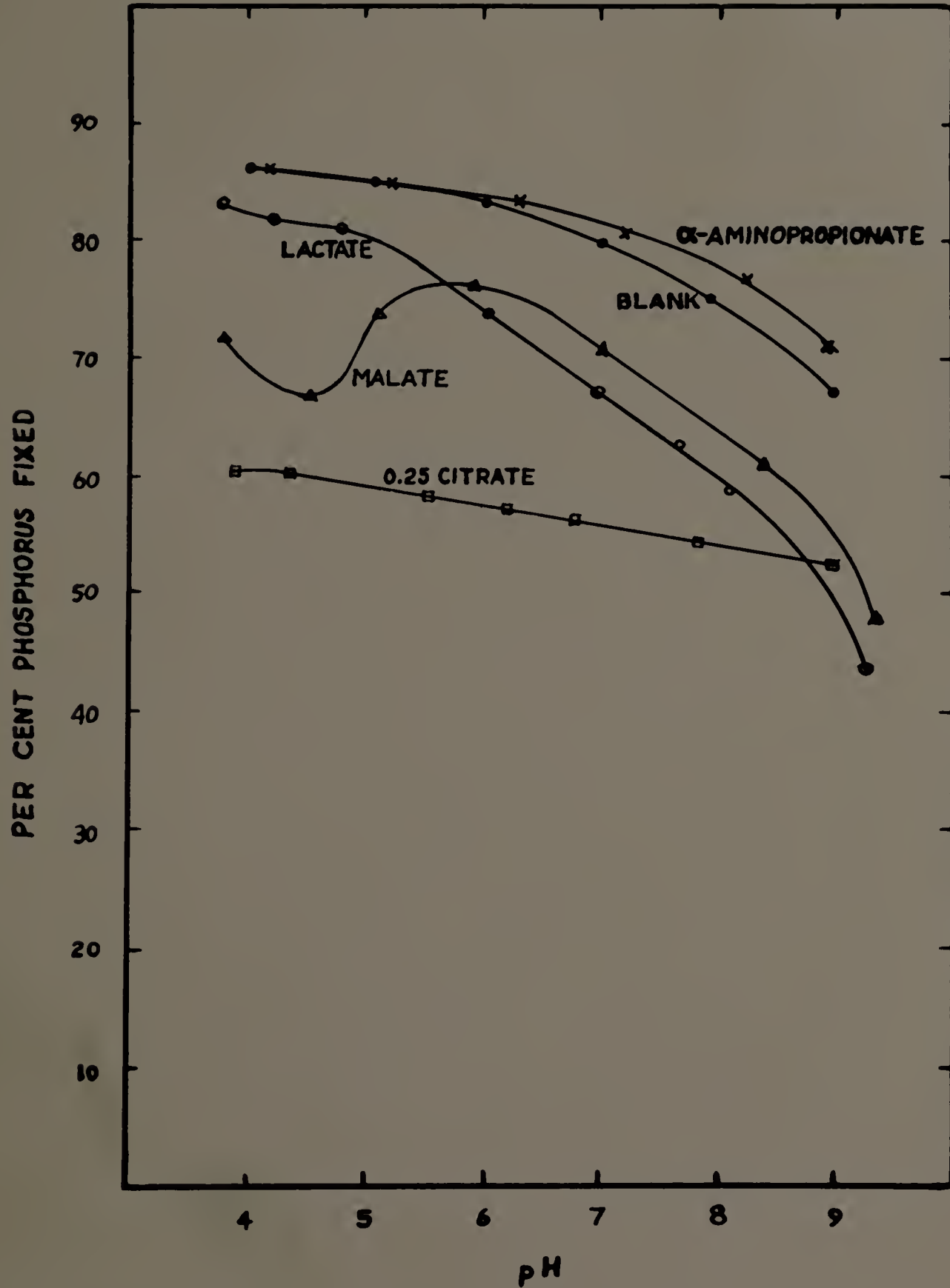


Figure 6. Influence of pH on the effectiveness of lactate, malate, α -aminopropionate, and citrate ions in preventing phosphate fixation by aluminum.

colloidal precipitate of aluminum phosphate was formed, but this could not be separated efficiently from the solution, so the reported quantity was used instead. The primary purpose of making this determination was to learn the shape of the curve so that it might be compared to that in the iron system shown in Figure 5. Such a comparison leads to the conclusion that the complexes formed in the two systems are not similar in nature. Differences in the curves shown for malonic acid and for tartaric acid in the two systems may be an indication that they are also complexed differently with iron than with aluminum.

Lytropic series of organic anions in the order of their efficiency to prevent the fixation of phosphate by iron or aluminum at various pH levels are presented in tables 7 and 8. It is noteworthy that throughout the pH range of acid soils, various organic acids were shown to have appreciable effect in reducing the fixation of phosphate by iron and aluminum. Many of these acids are known to be products of microbial decomposition of organic materials. From these considerations, the conclusion is drawn that the incorporation of actively decomposing organic matter in a soil would effectively increase the amount of phosphate available to plants.

Table 7

Lyotropic series of organic acids in the order of their efficiency at various pH levels to prevent phosphorus fixation by iron

| pH: 3 | 4 | 5 | 6 | 7 | 8 |
|-----------|-----------|-----------|-----------|-----------|-----------|
| Citric | Citric | Citric | Citric | Citric | Tartaric |
| Oxalic | Oxalic | Oxalic | Oxalic | Oxalic | Lactic |
| Tartaric | Tartaric | Tartaric | Tartaric | Tartaric | Citric |
| Malonic | Malic | Malic | Malonic | Lactic | Malonic |
| Lactic | Malonic | Malonic | Lactic | Malonic | Oxalic |
| Malic | Lactic | Alanine | Alanine | Alanine* | Succinic* |
| Alanine | Alanine | Lactic | Malic | Malic* | Malic* |
| Aspartic* | Aspartic* | Aspartic* | Succinic* | Succinic* | Alanine* |
| Succinic* | Succinic* | Succinic* | Aspartic* | Aspartic* | Aspartic* |

*Fixation equal to or greater than that when anion was absent.

Table 8

Lyotropic series of organic acids in the order of their efficiency at various pH levels to prevent phosphorus fixation by aluminum

| pH: 4 | 5 | 6 | 7 | 8 | 9 |
|----------|----------|----------|----------|----------|----------|
| Citric | Citric | Citric | Citric | Citric | Citric |
| Oxalic | Oxalic | Oxalic | Lactic | Lactic | Lactic |
| Malonic | Malonic | Malonic | Oxalic | Malonic | Tartaric |
| Malic | Malic | Lactic | Malonic | Tartaric | Malonic |
| Tartaric | Tartaric | Tartaric | Tartaric | Malic | Malic |
| Lactic | Lactic | Malic | Malic | Succinic | Succinic |
| Succinic | Succinic | Succinic | Succinic | Oxalic | Oxalic |
| Aspartic | Aspartic | Aspartic | Aspartic | Aspartic | Aspartic |
| Alanine* | Alanine* | Alanine* | Alanine* | Alanine* | Alanine* |

*Fixation equal to or greater than that when anion was absent.

SUMMARY AND CONCLUSIONS

1. A lyotropic series of certain organic anions in the order of their efficiency to prevent the fixation of phosphate by iron and aluminum at various pH levels was established by the use of pure solutions.
2. At various levels throughout the pH range of acid soils various organic anions were shown to markedly reduce phosphate fixation. Some anions were most active in this capacity at low pH values, some at high, and others at intermediate levels.
3. Citrate ion was the most effective anion studied. It was considerably more active in the prevention of phosphate fixation by aluminum than by iron.
4. The efficiency of organic anions in this capacity was found to increase with an increase in the number of carboxyl and hydroxyl groups, and with their proximity in the molecule; it was found to decrease with the length of the carbon-chain.
5. Amino acids were found to be ineffective in preventing phosphorus fixation by iron or aluminum at any pH value.

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