THE EFFECT OF THE PRESENCE OF PHOSPHATES ON THE ADSORPTION OF ACID DYES BY MORDANTS.

By

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THE EFFECT OF THE PRESENCE OF PHOSPHATES ON THE ADSORPTION OF ACID DYES BY MORDANTS.

INTRODUCTION.

Salts have long been used in the dye baths for the purpose of restraining or assisting the dyeing process. Sulfates, chlorides and phosphates have possibly found more general use than any others. Many attempts have been made to advance a satisfactory theory to explain the effect of these salts upon the dyeing process but none of these have proven entirely satisfactory. The reason for this seems to be the lack of quantitative data based on investigations in which all of the variables affecting the dyeing process have been controlled. No one theory of dyeing has been found adequate to explain all of the different methods of attaching the dye to the desired medium. Hence, it is possible that it may be necessary in explaining the action of salts to have a different theory for each class of dyeing.

Recently it has been shown that the dyeing of mordants of the type of hydrous ferric oxide and hydrous aluminum oxide with acid dyes is a pure chemical reaction in which the dye forms a compound with the mordant.[4] Since this is established it was thought that a reasonable theory for the action of salts in the mordanted dye baths might be evolved.

The object of this piece of work was to obtain quantitative data on the effect of phosphates in the adsorption of acid dyes by mordants and, on the basis of this, to arrive at some satisfactory explanation for their behavior.

HISTORICAL REVIEW.

In the dyeing process two general classes of color substances are used: those which will dye the fiber directly, and those which will only dye a material mordanted with a metallic salt or hydroxide or with the addition of a metallic salt to the dye bath. The first class has been named by Edward Bancroft in his "Treatise on Dyeing", "Substantive Dyes" and the latter, "Adjective Dyes". Knecht in his "Manual of Dyeing" tells us that "in a pure state the adjective dyes are only slightly colored and when used alone in dyeing they give rise to worthless results. But when used in conjunction with metallic mordants such as salts or iron, chromium, aluminum or tin intensely colored insoluble compounds-so called color lakes- are produced in the substance of the fiber which thus becomes dyed." Similar color lakes can be produced without the presence of the fiber by adding the metallic salts to solutions of the colouring matter or by treating hydroxides of the metals with solutions of the dye under suitable conditions.

Mordant is the name applied to the class of substance which are used to fix adjective dyes on the fiber. The term is derived from the French "mordre" meaning to bite or corrode. According to Knecht[2] the early French dyers believed that the utility of the metallic salts they employed consisted in their corrosive nature. It was thought that these substances opened the pores of the textile fibers and thus rendered them more capable of adsorbing the dyestuff. At a later period, he states, it was recognized that the so-called mordants entered into a chemical combination with the dyestuffs and formed insoluble compounds or color lakes. W. D. Bancroft[3] disagrees with this point of view and contends that the dye is merely adsorbed by the mordant and forms a colloidal lake. Gordon and Marker[4], on the other hand, have shown that certain dyes form definite compounds with both iron and aluminum mordants. In order to distinguish them from other compounds which are added to the dye bath and which do not take any part in the ultimate color, mordants are considered substances which partly or wholly combine with the dyestuffs and fix them on the fiber.

Mordants may be classified as acid or basic. The acid mordants, of which the tannins and fatty acid compounds are the most important serve for the fixation of basic dyestuffs and metallic oxides. They are often used for fixing basic mordants on the fiber which then act as the true mordants in dyeing. Their chief use is in the dyeing of cotton and linen and in weighting silks.

The basic mordants contain the hydrated oxides of the heavy metals as their active constituents[2], of this class the most important are compounds of aluminum, chromium, iron, copper, and tin. These mordants serve for the fixation of acid dyestuffs. Sometimes a double mordant is found desirable, in which case the oxides of magnesium, zinc, cobalt and nickle are mixed with those mentioned above.

The process of dyeing, with a mordant is carried out in acid, alkaline, or neutral bath depending upon the material to be dyed and the dyestuff used. Cotton is generally dyed in alkaline bath and wool in neutral or acid bath. The temperature employed and the time allowed for the operation also depends upon the material to be dyed. Generally a boiling solution is used and the process carried on for one hour.

Different methods are used for making the metal compound attach itself to the fiber. The composition of the mordant in the fiber then will vary with the fixing process. Aluminum occurs almost always as a hydroxide either from hydrolysis of its salt or ammonium hydroxide may be added to hasten the action. Phosphates and arsenates are often added for the purpose of fixing the metal, in which case the mordant will contain some of the metal phosphate as well as the hydroxide.

Besides the materials mentioned above it is common practice to add to the dye bath various salts, acids, and bases, which have for their purpose assisting or restraining the dyeing process. Sodium sulfate, sodium chloride and sodium phosphate are the salts often used, and at times almost all of the common acids have been employed, sulphuric, acetic and formic are possibly chief among these. When sulphuric acid is used with acid dyes it increases the rate of adsorption on wool very greatly and sodium sulphate is added to decrease this, thus assuring a much more even distribution of the dye on the fiber. J. K. Wood[5] in his "Chemistry of Dyeing" attempts to explain this action by saying that the acid reacts with the salt of the dye to form the free colour acid which is taken up by the fiber. The hydrogen ion of the sulphuric acid would by the common ion effect decrease the solubility of the color acid. The addition of sodium sulfate causes sodium acid sulfate to be formed, which decreases the hydrogen ion concentration and thus decreases the rate of adsorption of the dye. It has been shown later that this conception is not true since the color acid does not dye any better or faster than the salt of the dye[8]. Bancroft[6] offers the following explanation: "Since sodium as an ion has a relatively slight effect on the adsorption and sulfate, as an ion, a relatively large one, it follows that sodium sulphate will cut down the adsorption of an acid dye and will tend to strip an acid dye which has already been adsorbed."

Possibly the first quantitative work published on the effect of salts on the adsorption of dyes is given by Pelet-Jolivet[7]. His work was carried out upon wool without a mordant present. In the following table he shows that both sodium acid phosphate and sodium sulphate increase the adsorption of methylene blue (a basic dye).

100 cc. Solution 1 gm. wool

Conc. Methylene Blue present	Methylene blue adsorbed		
	no salt	0.06N Na_2SO_4	0.06N Na_2HPO_4
0.1	35	45.6	81.1
0.2	40	52.2	91.3
0.3	43	56.4	95.6
0.4	44	59.4	98.6

It is thus seen that sodium phosphate is the most effective in increasing the adsorption of the dye. Since the sodium ion is common to both salts the effect is presumably due to the different influences of the sulfate and phosphate ions. Pelet-Jolivet also studied the effect of different cations on the adsorption of dyes by wool and silk. His results show that silk took up 13.3 mg. of methylene blue from a solution containing sodium chloride and only 6.3 mgm. from a solution containing barium chloride. With wool the adsorption of methylene blue decreases with addition agents in the following order; sodium phosphate, sodium sulfate, no addition barium chloride, and platinum tetrachloride. In summing up these experiments, Pelet -

Jolivet makes the following observation: "From these experiments it is clear that the negative SO_4^{--} and PO_4^{---} ions have increased the dyeing of methylene blue while the positive ions of barium and platinum have decreased it. The ions of the electrolyte act on dyeing as they do on the precipitation of colloids since they follow the valency rule." It will be observed that these results do not take into account the effect of the alkalinity of the solution which is increased by the sodium monohydrogen phosphate and not by the sodium sulfate. Methylene blue is adsorbed much greater in an alkaline solution than in an acid or neutral; this would account for some of the effect ascribed to the phosphate ion. Although, as will be shown later the phosphate ion does have a decided influence.

In the adsorption of acid dyes Pelet-Jolivet found the effect of addition agents to be exactly opposite to that in basic dyes. He first carried out experiments using different acids to furnish the negative ions. (loc. cit.)

5 grams wool. 200 cc. Crystal Ponceau (acid dyes)

	Mgm Crystal Ponceau adsorbed.		
cc N/10 acid	HCl	H_2SO_4	H_3PO_4
6	44	42	42
8	109	93	48
18	158	104	80
28	171	153	102

In this case the decrease is in the order of hydrochloric, sulphuric, phosphoric acid. But this comparison is not entirely true since these acids do not give the same hydrogen ion concentration and this has been shown by Reinmuth and Gordon,[9] Briggs and Bull,[10] and Gordon and Marker[4], to be a very important factor. The next experiment taken from Pelet-Jolivet overcomes this objection by adding a neutral salt to the bath of an acid dye. I am taking the liberty to quote the experiments directly both from a historic viewpoint and as will be seen later they have a direct bearing upon the theory of the action of the negative ion of the addition agent.

5 grams wool, 200 cc. Crystal Ponceau solution.

% dye sol.	a Mgm. dye adsorbed		
	3 cc. .1N H_2SO_4	.12 gm Na_2SO_4	Without addition
1	65	36.2	41.7
2	113	59.8	62.8
3	150	64.8	76.5
4	178	70.8	86.5

2 grams wool in 200 cc. 5% Crystal Ponceau.

Addition to bath	Ads. dye in mgm.
0.3 gm Na_2SO_4	11.4
0.3 gm Na_2HPO_4	0.0
0.3 gm $PtCl_4$	20.0
without addition	13.1

The increase in the adsorption with sulphuric acid is due to the increase in the hydrogen ion concentration of the solution. The effect of the salts in the order of the amount of acid dye adsorbed is $PtCl_4$ $>$ none $> Na_2SO_4 > Na_2HPO_4$. It should be noted that some of the effect of the phosphate is undoubtedly due to the effect of the salt decreasing the hydrogen ion concentration of the bath.

The general conclusions which Pelet-Jolivet draws from this experimental evidence is interesting: "The ion with the sign opposite that of the dye increases the dyeing, the ion with the like sign decreases it. Multivalent ions have stronger effect than univalent ones." He further concludes that the fiber acts as if it were a gel and the dye a colloid and the result of the addition of salts is the same as with other colloidal precipitations as found by J. Perrin.

D. B. Lake[10] in experiments carried out in his studies of dyeing and cleaning confirms the results of Pelet-Jolivet quoted above. But he likewise failed to control the hydrogen ion concentration of his dyebath. Hence his results do not show the true effect of the addition agents.

Although Pelet-Jolivet in 1910 made the

observation that an increase in the hydrogen ions in the dye bath lessened the dyeing of a basic dye and increased that of an acid dye, and also stated that this action was proportional to the hydrogen ion concentration; no work was reported where the hydrogen ion concentration of the dye bath was controlled, while additions were made, until that of Briggs and Bull[11] in 1922. In a series of experiments in which they carefully controlled the hydrogen ion concentration of the dye bath while adding assistant and restraining salts, they obtained results which were in effect very similar to those of Polet-Jolivet. For example they found that at a PH of 4.0 the amount of Lake Scarlet R (an acid dye) adsorbed by wool in the presence of hydrochloric acid was 48 mg., in the presence of phosphoric acid was 46.5 mg., and in the presence of sulphuric acid 30 mg., the order being $HCl > H_3PO_4 > H_2SO_4$. Briggs and Bull attribute this decrease to the negative ions in solution. Phosphoric acid, they claim, yields $\bar{H}_2PO_4$ ions, and consequently does not have as great a restraining influence as does the divalent $\overset{=}{SO}_4$ ion from sulphuric acid. With the same dye they found that if hydrochloric acid was used with equal molar quantities of sodium chloride and sodium sulphate, the wool adsorbed more dye from the sodium chloride bath.[12] If this effect was merely a colloidal phenomenon due to the charge on the anions in solution it would seem that the action of these two should be the same inasmuch as there are just twoce as many monovalent chloride ions in solution as there are divalent sulfate ions. They explain this by saying that the sulfate ion is adsorbed on the wool more strongly than the chloride and hence has greater effect in preventing the dye from being taken up.

With Orange II dye (acid dye) and wool Briggs and Bull obtained results similar to those with Lake Scarlet R. At the same PH value more dye was adsorbed by the wool in the presence of hydrochloric acid plus sodium acid phosphate and least of all with sulphuric acid plus sodium sulphate. These writers state that their results are in accord with the adsorption theory of dyeing which was summarized and elaborated by Bancroft.[3]

They give this briefly as follows: "When any fiber is placed in a dyebath, it may adsorb any or all of the constituents of the bath. (In the case of acid dyes in acidified baths these constituents are hydrogen ions, sodium ions, anions of the dye, anions of the acid and undissociated compounds). Hydrogen ions being in general, more strongly adsorbed than other univalent cations will be taken up largely and the fiber will become positively charged relative to the solution. This positive charge in turn will lead to an increased adsorption of anions, and by this secondary process of adsorption the charge on the fiber will be more or less neutralized. The anions of the dye and acid will both be taken up in amounts which are determined for a given fiber by the nature of the ions and their concentrations. Since, in being adsorbed, the anions of an acid dye have to compete with the other anions of the bath it follows that the addition of other strongly adsorbed anions will decrease the amount of dye taken up. In a similar way, the addition of a strongly adsorbed cation will cause an increase in the amount of acid dye taken up, other factors remaining constant."[13]

Since hydrated oxides of the metals used as mordants seem to take up dyes very similar to the manner in which wool takes them up, it might be thought that the addition of salts would have a similar effect in both cases. Gordon and White[14] have shown this to be true. Phosphates were found to decrease the adsorption of acid dyes by the hydrated oxides of iron and aluminum. The adsorption of basic dyes was found to increase on the addition of phosphates. Later Wood and Woller[15] have presented data which confirms these results with hydrated aluminum oxide. Similar cases were observed by Lachs and Michalis[16] and have been explained as due to the presence of a readily adsorbed anion causing greater adsorption of the cation.

Many attempts have been made to explain the action of salts in dyeing, each of course depending upon the special theory of dyeing to which the author happened to hold.

In the adsorption theory of dyeing as outlined above it is thought that the effect of the salt is one of preferential adsorption. With a highly adsorbed anion present, this will be adsorbed in preference to the dye. But even Pelet-Jolivet who is a great exponent of this theory points out that it will not hold in all cases. For when an ion increases the adsorption of the dye under this theory it is supposedly due to the colloidal precipitation by the ion of the dye colloid. In an experiment he showed that benzopurpin is precipitated with calcium chloride while trypanrot, a sulfonate of benzopurpin, a likewise highly colloidal dye, is not precipitated. Pelet-Jolivet suggests that the action of the salt may be due to the following reaction:

$$2ANa \text{ plus } CaCl_2 = A_2Ca \text{ plus } 2NaCl.$$

Where A. represents the dye ion. In order to substantiate this theory he carried out an experiment in whcih he observed the reaction between the salts:

sodium chloride, sodium sulfate, sodium phosphate, potassium ferricyanide, barium chloride and sodium carbonate and a series of twenty or more dyes. His conclusion was in the case of acid dyes that the cation of the salt which caused increased adsorption actually combined with the dye forming a less soluble salt.

In the case of substantive dyes Briggs[17] explains the dyeing as a distribution between the interface and the suspending medium. The action of the salt is to either stabilize or destabilize the suspension of the dye.

Boeseken, Tergau and Bennendjk[18] in investigating the action of salts on the dyeing of cellulose with benzidine colors show that the action is similar to the salting out of soaps. The quantity of electrolyte necessary for the precipitation is considerably more than equimolar. 1/68 millemole of benzopurpin required 40 millimoles of Glaubers salt. The influence of sulfates of the metals was found to be in the following order: NH_4, Li, Na, K, Mg, Cd, Zn, Al, Cr, Fe. Within certain limits they conclude the quantity of the dye fixed upon the fiber is proportional to the amount of electrolyte.

G. T. Morgan[19] has proposed a theory of dyeing based on Werner's coordination theory. He explains the formation of color lakes by the formation of coordination compounds between the dye and the metal.

Knecht[20] has possibly been the greatest exponent of the chemical theory of dyeing. He assumes that all fibers or mordants possess either acid or basic properties and all dyestuffs possess either acid or basic properties or represent the salts of acids or bases. The dyeing process is then one of salt formation between the dye and the fiber or the dye and the mordant. Knecht infers from experiments that the chief function of the acid in dyeing animal fiber is to produce a lake yielding substance during the process of dyeing. Fort[21] holds to this same idea and on this theory explains the action of salts. For the dyeing process Fort gives the equations:

Wool plus H_2SO_4 = wool .H_2SO_4

Wool .H_2SO_4 plus color acid Na = wool base-color acid plus Na_2SO_4 or

Wool base H_2SO_4 plus color acid = wool base-color acid plus H_2SO_4 . He has found that one mole of dye acid will displace one mole of sulphuric acid from wool which has been previously treated with sulphuric acid. He points out that the reaction of the dye with wool can be compared to the action of a dye on magnesium or magnesium oxide. The action of the color acid of Crystal Scarlet on magnesium is very slow, only after several days was the metal coated with the magnesium -dye salt. With sulphuric acid present the action is very fast due to the formation of magnesium sulfate. The salt will react quantatively very rapidly with the dye to form the magnesium salt of the dye. The sodium salt of Crystal Scarlet does not react with magnesium oxide; if sulphuric acid is added it does so very rapidly due to the formation of magnesium sulphate. Fort states that the stripping effect of sodium sulfate of dye from cloth is merely a reversal of the action given above. He also states that when mordants are used the same theory holds.

More recently Rossi and Basini[22] have attempted to show that the salt formation theory and the solution of the dye in the fiber theory will not explain the known facts of dyeing. They claim that the fiber acts as a true coagulating agent like Al_2O_3 and both coagulates and adsorbs the dye.

We find many references in the literature where the authors have believed chemical compounds to have been formed between the dye and the mordant. But it remained for Gordon and Marker[23] to prove that these compounds actually exist. In dyeing aluminum and iron mordants with Orange II dye, they isolated compounds having the formula AlX_3 and FeX_3, where X represents the dye radical.

Bayliss[24] has recorded a case where he believes chemical reaction of the dye and mordant was preceded by adsorption. When a dilute colloidal solution of the blue color acid of Congo Red was mixed with aluminum hydroxide, the latter adsorbed the color acid and acquired a blue color. On suspending the blue precipitate in water and warming, the color changes to red owing to the formation of an aluminum salt.

Wedekind and Remboldt[25] have described a similar experiment. They show that the basic gels of aluminum, iron, chromium and zinc adsorb dye acids and then give characteristic red colored salts on heating. They state that this is chemical action preceded by adsorption. The dyes used in this were Benzopurpin 4B and 10B, Benzo Orange R, and Congo Corinth G and B.

Since it has now been shown definitely by Gordon and Marker[23] that the taking up of dyes by mordants is a pure chemical reaction, we propose to show by the experimental work that follows, that the effect of phosphates in decreasing the dyeing of mordants with acid dyes is also due to chemical reaction.

EXPERIMENTAL.

Materials Used:-

The hydrous oxide gels of iron, aluminum and chromium were used throughout the experiment. These were prepared by disolving seventy-five grams of the respective chlorides in five liters of water at a temperature of fifty degrees centigrade and then very dilute ammonium hydroxide was added until all of the metal had precipitated. The gel was washed free from chlorides by decantation. This usually required six or seven days. In most of the experiments the gel was used mixed with such a quantity of water that it could be readily drained free from a fifty cubic centimeter pipette from which the tip had been cut off in order to allow passage of the large particles of gelatinous material. This method of measuring the amount of gel was used in all but one experiment. Where it was objectionable to have such a large quantity of water present the gel was filtered by suction until all the water possible had been removed. The gel in the resulting condition was weighed up on the balance in a stoppered weighing bottle. The silica gel was furnished by the Davidson Chemical Company. Before using it was ground small enough to pass a one hundred mesh sieve washed by decantation and allowed to dry at room temperature.

The water content of the gel was determined by heating a sample for twenty-four hours at 105° C. The iron, aluminum, and chromium gels that were in a condition to be measured in a pipette contained about 98 % water.

The dyes used were donated by E. I. du Pont de Nemours and Company. The acid dye, Orange II is a sodium salt and the basic dye Crystal Violet is a chloride. Potassium di-hydrogen phosphate; the salt added was J. T. Baker, C. P. material.

Experimental Proceedure.

In the adsorption of dyes by gels Gordon and Marker[4] have shown that equilibrium is reached if the dye and the gel are heated to 100° C for two hours with frequent shaking. Gordon and Starkey[26] have shown that in order to obtain maximum adsorption of potassium de-hydrogen phosphate by inorganic gels the mixture must be shaken almost continuously for seventy two hours. Thus when it was desired to have comparable results with both the dye and phosphate, the solutions were put into 250 cc. ground glass stoppered bottles, heated at 100° for two hours, then shaken continuously for three days in a mechanical shaker.

After this the solution was analyzed for materials unabsorbed. The solution was separated from the gel by an ultra filter. This was made by pouring the mixture of gel and solution over a filter paper until the paper had become thickly coated with gel. The whole solution was then filtered through this.

Determination of adsorbed Materials.

The adsorption was determined by analyzing the solution before mixing with the gel and then again after adsorption had taken place. The difference between these determinations was called the amount of material adsorbed. The dye was determined by titration with titanium trichloride according to the general directions in Knecht and Hibberts Manual of Volumetric Dye Analysis. Specific directions were furnished by E. I. Du Pont de Nemours and Company. Their directions are as follows:

"DuPont Orange II: Dissolve .2 gms. dye in 100cc water and 35 cc of sodium tartrate (25%). Boil gently three minutes and titrate hot under CO_2 with .05N $TiCl_3$. The end point is the final color change from a light pink to a colorless solution."

"DuPont Crystal Violet: Dissolve .5 gms. dye in 50 cc water and 50 cc of alcohol, add 50 cc of 25% sodium tartrate solution, boil gently three minutes and titrate hot under CO_2 with .05N $TiCl_3$ solution. The final color change is from red to gray or brown and is sharp. The titration should be carried out slowly as the end point is approached."

In determining potassium, and the phosphate radical in Orange II solutions, it was necessary to first remove the dye by precipitation with HCl or to decompose it by boiling with aqua-regia. Both methods were used and the latter found to be the most satisfactory. The potassium was determined by precipitation with platinic chloride according to the Lindo Gladden method. The phosphate was determined by the ammonium molybidate method. In the case of Crystal Violet the dye was removed by precipitation with sodium hydroxide.

Determination of the Hydrogen Ion Concentration of Solutions Used.

The hydrogen ion concentration of all clear solution was determined by means of the Bailey Electrode. A normal calomel electrode was used with this and the readings taken on a Leeds and Northrup "Student Type" potentiometer.

In order to obtain the Ph of the dye solutions and of solutions containing any colloidal material a modified form of the Hildebrand type electrode was used. The electrode was a single platinum wire coated with platinum black. Before using this it was saturated with hydrogen by electrolysis in a sodium hydroxide solution. It was found that this treatment insured much steadier readings in dye solutions. In making a determination the solution was saturated with hydrogen before the electrode was immersed in it. For

Crystal Violet solutions and clear solutions the readings of this electrode could be checked with those of the Bailey electrode. But with Orange II solutions this is not true. With Orange II all readings were determined in duplicate on the electrode described above as soon as a steady reading could be obtained after the electrode was immersed in the solution. While it is not claimed that these values are absolute, they are the best it is possible to obtain under these conditions and they allow excellent comparison for this work.

EXPERIMENTAL RESULTS.

The data on the adsorption of Crystal Violet (a basic dye) which were presented at the Washington meetin of the American Chemical Society[14] are tabulated here to show the contrast in the effect of the phosphate addition to an acid dye and to a basic dye. This will be referred to as confirming the theory of the action of phosphates in dye baths to be presented later and it is desirable to have it at hand for reference. As would be expected the results with the basic dye are directly opposite to those with the acid dye.

The following tables show a comparison of the Crystal Violet dye adsorbed with KH_2PO_4 present and when no salt was used. In these experiments the PH was varied by using sulphuric acid and sodium hydroxide. The solutions used were .5% dye and $.5NKH_2PO_4$.

TABLE I.

The Effect of Phosphates on the Adsorption of Crystal Violet (a basic dye) by Silica Gel.

Ph of salt solution	Ph of bath after ads.	Mgm. of dye ads. per gm dry gel	
		With KH_2PO_4 present	no salt present
1.1	1.05	1.1	1.1
1.42	1.52	2.3	2.4
2.74	2.75	2.5	3.1
4.62	3.14	3.2	4.1
4.67	3.16	3.5	4.2
6.68	4.43	7.3	4.6
6.98	4.70	9.0	4.7

TABLE II.

The Effect of Phosphates on the adsorption of Crystal Violet (a basic dye) by Aluminum Gel.

Ph of salt solution	PH of bath after ads.	mgm. dye ads. per gm. dry gel:	
		KH_2PO_4 present	without salt[4]
1.52	2.91	---	3.0
2.81	5.36	49.2	4.0
4.63	5.98	173.4	7.0
6.12	6.12	216.5	13.0
6.49	6.30	439.3	16.0
6.85	6.54	449.1	18.0

TABLE III.

The Effect of Phosphates on the Adsorption of Crystal Violet (a basic dye) by Iron Gel.

PH of salt solution	Ph of bath after ads.	mgm. dye ads. per gm. dry gel.	
		KH_2PO_4 present	without salt[4]
2.59	5.27	378	28.0
4.45	6.04	460.9	40.0
6.12	6.14	906.8	46.2
6.49	6.42	1041.4	47.5
6.85	6.81	1118.3	48.0

It is seen from the above data that the effect of the phosphate salt added is to increase the adsorption of the basic dye. The PH could not be carried any higher due to the dye precipitating out of solution. The tables show that when the basic dye is added to the bath the PH is lowered. This is caused by the hydrolysis of the dye. Crystal violet is a salt of a strong acid (HCl) and a weak dye base. Hence the effect will be to lower the PH of the solution to which it is added. Iron gel seems to be the best adsorbant for the basic dye and as will be noted in the following tables it is also the best adsorbant for phosphates. Both the potassium and the phosphate adsorbed in the above experiment were determined. The data is for all three gels.

TABLE IV.

The Effect of Crystal Violet Dye on the Adsorption of Potassium Acid Phosphate adsorbed by Silica Gel.

PH of bath after ads.	mgm. adsorbed per gram of dry gel.			
	PO_4 ads. dye present	PO_4 ads. no dye[26]	K ads. dye present	K ads no dye[26]
1.05	-0.8	2.7	-0.2	-2.7
1.52	-0.6	0.5	-0.2	-2.4
2.75	-0.5	-0.3	-0.16	-1.6
3.14	-0.1	-0.1	-0.13	-1.4
3.16	0.1	-2.0	0.01	-1.5
4.43	0.2	-2.3	0.5	-0.2

TABLE V.

The Effect of Crystal Violet Dye on the Adsorption of Potassium Acid Phosphate by Aluminum Gel.

PH of bath	mgm. adsorbed per gram of dry gel.			
after ads.	PO_4 ads. dye	PO_4 ads.	K ads. dye	K ads.
2.91.	present	no dye[26]	present	no dye[26]
2.91	127.8	318.5	4.4	4.7
5.56	124.9	240.0	[illegible]	9.4
5.98	110.9	233.0	11.4	10.6
6.12	101.2	227.5	9.4	10.8
6.30	104.3	223.3	9.5	11.1
6.54	98.3	218.0	9.9	11.5

TABLE VI.

The Effect of Crystal Violet Dye on the Adsorption of Potassium Acid Phosphate by Iron Gel.

PH of bath	mgm. adsorbed per gram of dry gel			
after ads.	PO_4 ads. dye	PO_4 ads.	K ads. dye	K ads.
	present	no dye[26]	present	no dye[26]
5.27	272.5	--	17.9	--
6.04	254.2	--	26.1	91.0
6.14	258.6	--	28.7	90.0
6.42	247.3	359.0	30.2	82.0
6.81	255.6	276.0	28.1	76.0

In every case it is shown that even though the dye is very much more highly adsorbed with the phosphate present, the PO_4 adsorption is decreased from normal. It may seem that the dye is preferentially adsorbed over the phosphate, but the difference in the phosphate adsorptions is not great enough to account for the high adsorption of the dye. It is believed that the salt increases the size of the dye particle to colloidal dimensions and then it is merely filtered out of solution by the gelatinous particles of metallic oxides.

It will be noted in subsequent data that the action of phosphates with acid dyes is directly opposite to that with basic dyes.

Adsorption of Orange II (an acid dye) by Silica, Iron, Aluminum and Chromium Gels.

With silica gel there was no adsorption of the acid dye Orange II either with or without a salt present.

The following table shows that with Aluminum Gel the adsorption of Orange II was greatly decreased by the presence of the phosphate. In this experiment the PH was varied with sulphuric acid and sodium hydroxide. The solution used was .5% dye and .05NKH_2PO_4.

TABLE VII.

The Effect of Potassium Acid Phosphate on the adsorption of Orange II by Aluminum Gel.

5% Dye and .05NKH_2PO_4.

PH of original salt solution	Final PH of bath	mgm. dye ads. per gm. dry gel. Phosphate present	no salt pres
2.68	5.05	53	279
3.13	5.51	26	186
3.38	5.43	27	185
4.48	5.73	15	177
6.49	6.02	14	170
7.02	6.56	1	166

This data is illustrated more vividly in Graph I.

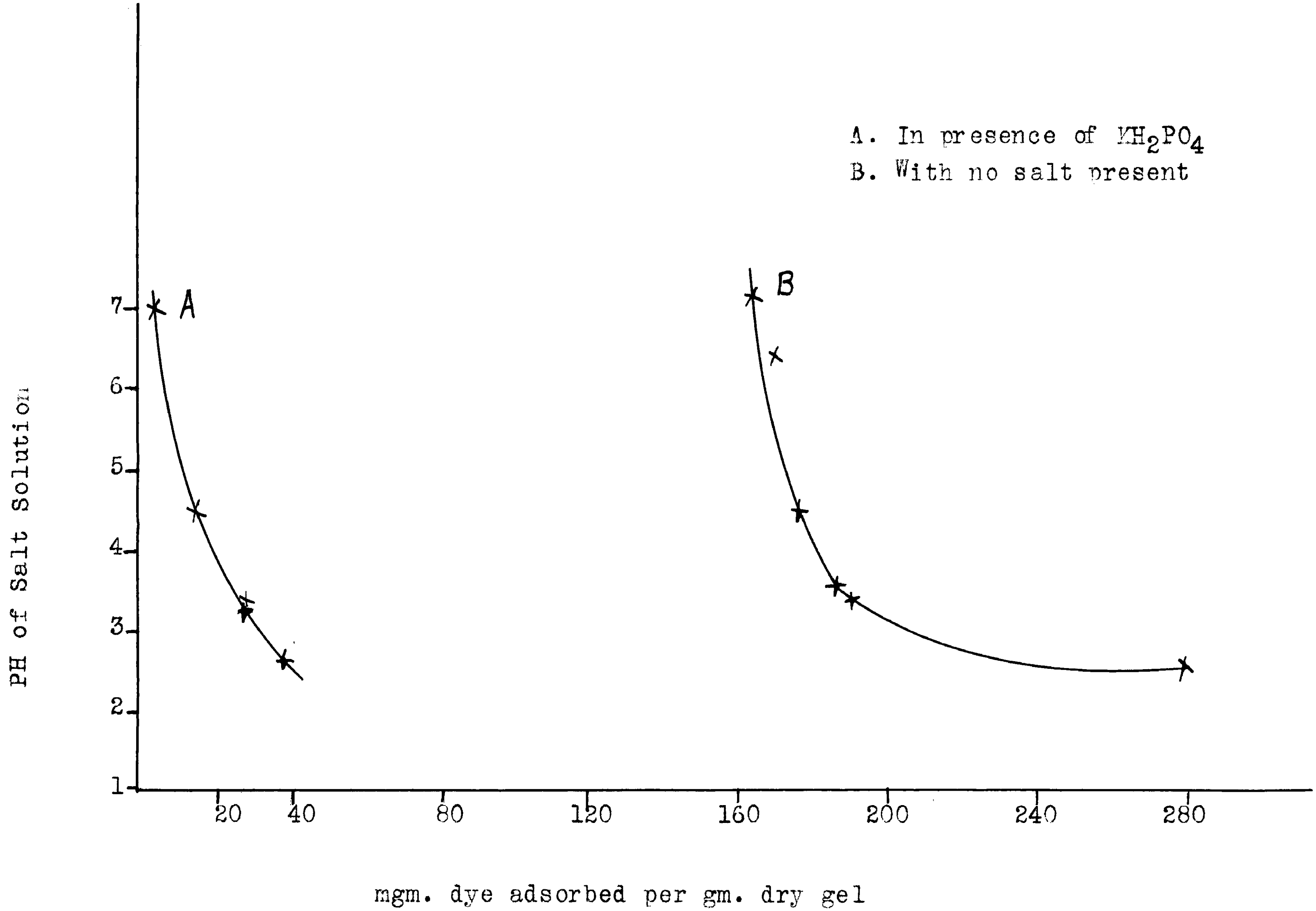
It is remarkable that the small amount of salt added to the dye bath should make such a marked decrease in the adsorptive power of the gel. It might be expected that the gel has preferentially adsorbed the phosphate, but the following data shows that there is also a great decrease in the phosphate adsorption.

TABLE VIII.

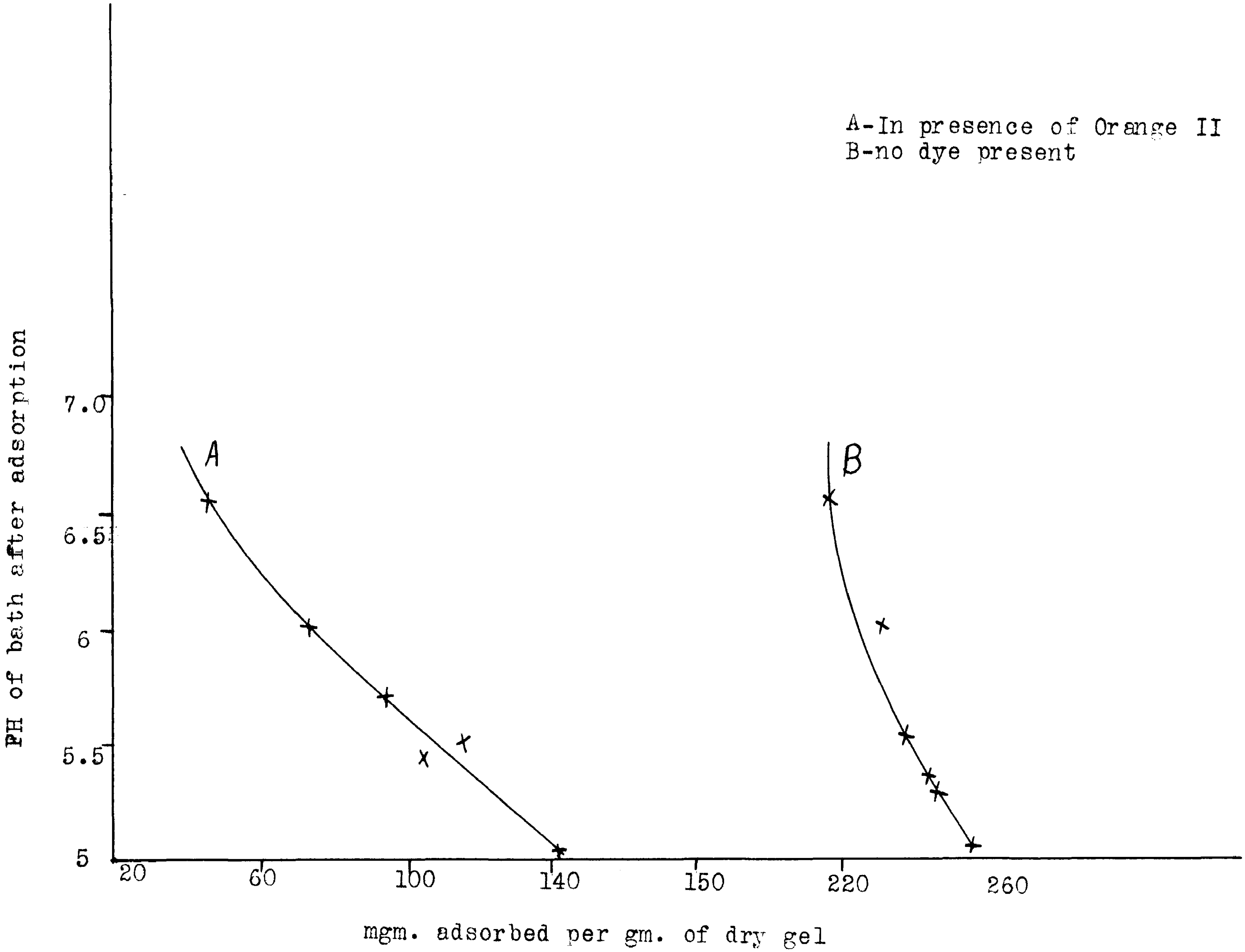
The Adsorption of Potassium Acid Phosphate by Aluminum Gel in the Presence of Orange II Dye

.5% Dye and $.05NKH_2PO_4$

PH of bath	mgm. adsorbed per gm. of dry gel			
after ads.	PO ads.dye present	PO_4ads. no dye[26]	K ads dye present	K ads no dye[26]
5.05	143.0	258.5	00	9.0
5.51	117.6	244.0	00	9.8
5.43	105.8	247.5	00	9.7
5.73	96.7	238.0	4.67	10.2
6.02	75.7	231.5	6.12	10.6
6.56	46.3	217.5	--	--



Graph I. Ads. of Orange II by Aluminum Gel.



Graph II Adsorption of Phosphate by Aluminum Gel

A comparison of the phosphate adsorptions is given in Graph II.

The great decrease in the adsorption of the phosphate cannot be balanced by the very slight adsorption of the dye. The same phenomenal decrease in adsorption is noted in the following data on iron gel.

TABLE IX

The Effect of Potassium Acid Phosphate on the Adsorption of Orange II by Iron Gel.

.5% Dye and .05NKH_2PO_4

PH of original salt solution	PH of bath after ads.	Mgm. dye ads. per gm.dry gel.	
		Phosphate pre.	No salt present
2.75	6.09	00	225
3.16	6.25	00	80
4.66	6.42	00	70
6.54	6.60	00	63
7.05	6.70	00	62

The phosphate and potassium adsorption was also decreased below normal even though no dye was adsorbed.

TABLE X

The Adsorption of Potassium Acid Phosphate by Iron Gel in the presence of Orange II Dye.

.5% Dye and .05N KH_2PO_4

PH of bath after ads.	mgm. ads. per gram of dry gel.			
	PO ads. dye present	PO_4 ads. no dye	K ads dye present	K ads. no dye
6.09	211.1	--	21.4	91.0
6.25	200.5	--	24.3	88.0
6.42	188.6	340	25.1	83.0
6.60	160.3	330	23.6	80.0
6.79	130.6	319	19.1	74.0

In order to determine whether this decrease in adsorption was due to the PO_4 ion alone or to other ions present, an experiment was run when phosphoric acid was added to the dye solution. Varying amounts of the acid were used in order to vary the PH. Of course there might be expected a change in adsorption due to the varying concentration of the negative radical. In the following experiment one gram of Orange II dye was dissolved in 200 cc of phosphoric acid solutions and added to 1.02 grams of gel.

TABLE XI

The Effect of Phosphoric Acid on the Adsorption of Orange II by Iron Gel.

Final PH of bath	mgm. per gram of dry gel.		
	PO_4 originally present	PO_4 ads.	Dye ads.
4.30	263.5	233.5	00
4.85	217.8	202.9	00
5.16	164.0	153.9	00
5.29	102.9	97.9	00
5.36	92.3	86.6	00
5.44	61.9	58.7	00

This table shows conslusively that the cutting out of the adsorption of the dye is due to the phosphate and not to the presence of other ions.

Having established the fact that the phosphate was the effective agent in decreasing the adsorption of the dye it became our problem to determine if possible just why the phosphate should do this.

Gordon and Marker[4] have shown that the taking up of Orange II by Aluminum and Iron gels is a chemical reaction and not merely a case of surface adsorption. According to this then the observed facts should offer explanation either on the basis that the phosphate is acting on the gel and preventing its reaction with the dye, or it is acting upon the dye in solution in such a manner that it prevents the reaction taking place.

Taking the latter idea first, it was thought possible that the phosphate might have an effect of increasing the solubility of the dye in solution and thus making its taking up by the gel more difficult. So an experiment was run to determine this. It was found that at the concentrations of phosphates used in the experiment there was no detectable influence upon the solubility. But if a large quantity of phosphate is added the solubility of the dye decreases and may be precipitated out of solution. This would have the effect of increasing the adsorption by gels rather than decreasing it. Another thought was, that owing to a change in the thermodynamic environment of the solution on the addition of phosphate it might take a longer time for the dye and gel to reach equilibrium. So an experiment was run in which the dye was allowed to remain in contact with the gel for a period of six months. Samples were removed at intervals for analysis.

Solutions of .5% Orange II Dye and .05 normal potassium dihydrogen phosphate were mixed with 1.08 grams of gel. This mixture was heated to boiling for four hours and placed in a mechanical shaker and agitated. This treatment was repeated at frequent intervals over a period of six months. The PH was varied with phosphoric acid and potassium hydroxide.

TABLE XII

The Result of Allowing Orange II and Phosphate Solution to Act on Iron Gel for a period of six months.

PH of dye bath Jan.1	PH of dye bath Jan.3	mgm. ads. per gm. dry gel.			
		Dye ads. Jan. 1	Dye ads. July 3	PO_4 ads Jan 1	PO_4 ads July 3
5.02	5.46	00	00	232.3	219.6
5.27	5.69	00	00	229.4	238.7
5.66	5.87	00	00	202.7	206.8
5.86	5.95	00	00	191.0	207.3
5.95	6.07	00	00	187.1	171.7
5.71	6.07	00	00	146.3	164.0

The data shows that there was no adsorption of dye under these conditions even after being in the presence of the gel for a period of six months. The phosphate adsorption changed only very slightly and the PH shows a correspondingly slight change. It was concluded then that the reason for phosphate cutting out the adsorption was not to be found in its effect upon the dye in the solution.

On the basis of the other idea mentioned above that the phosphate decreased the adsorption of acid dyes because of its effect upon the gel, it was thought possible that the phosphate might be adsorbed on the surface of the gel and thus prevent the gel reacting with the dye.

In order to determine this it was decided to run an experiment in which the gel would be allowed to adsorb the phosphate from the solution before adding the dye. If no adsorption took place it was thought it might be concluded that the phosphate coated the gel in such a way as to prevent its reacting with the dye.

.5 gram of gel and 100 cc of potassium di-hydrogen phosphate was boiled for two hours then shaken for three days in a mechanical shaker. 25 cc. of the solution was then removed and tested for phosphates.

Then 100 cc of a 1% dye solution was added and the mixture again boiled and shaken the same as before. The following results were obtained:

TABLE XIII

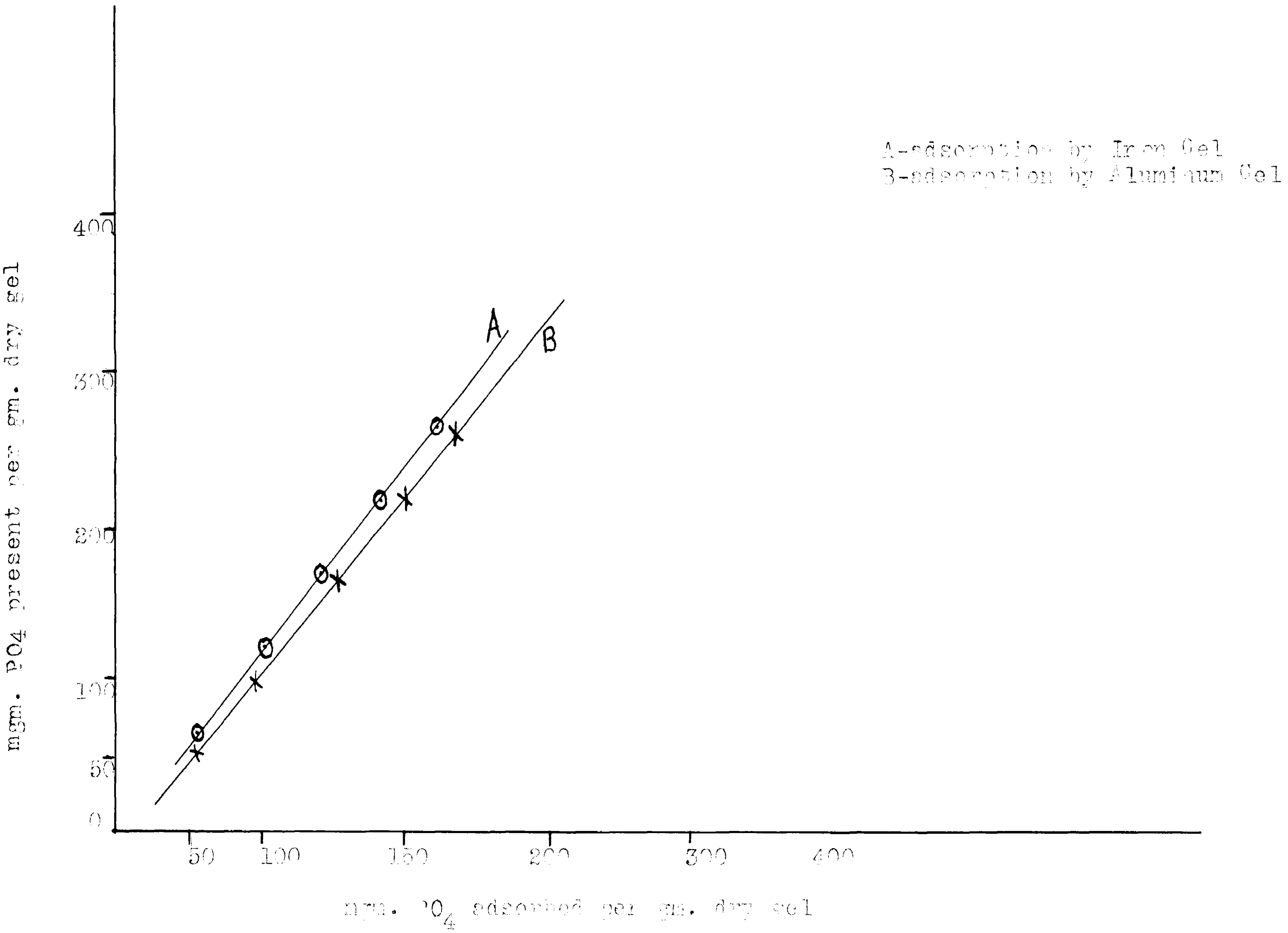
The Effect of Iron Gel Adsorbing all the Phosphate from the solution first, then adding Orange II.

Final PH of bath	Orig. PO$_4$ mgm per gm dry gel	PO$_4$ in supernatent liquid before dye added	Dye ads	PO ads. mgm per gm dry gel in final bath
5.53	63.7	none	00	59.4
5.73	127.4	trace	00	105.4
5.75	190.1	quantity	00	126.8
5.86	254.8	quantity	00	154.7
5.27	63.9	none	00	59.7

It will be noted that there was no dye adsorbed even when there was no phosphate in the supernatent liquid when the dye was added. The data shows, though, that some of the adsorbed phosphate was released to the solution after the dye was added. This might have been expected, since in Table XI it was shown that in the presence of Orange II the amount of phosphate adsorbed is proportional to the concentration of the solution. Hence when the solution was diluted with the dye we would expect some of the phosphate to be released. This point is illustrated in Graph III.

Since some phosphate was released to the solution this experiment does not prove conclusively its original purpose. It does show though that the dye will not replace the adsorbed phosphate on the gel. It became important then to know if the dye was adsorbed first would the phosphate displace it. In order to determine this the following experiment was preformed:

150 cc of a .75% solution of Orange II was boiled with the gel for two hours and samples were removed for analysis. 100 cc of $.05NKH_2PO_4$ was then added to each solution. This was then shaken for three days to attain equilibrium. The PH of the original dye solutions were varied by adding sulphuric acid and sodium hydroxide. The results of this experiment are given in tables 13 and 14.



Graph III. The Relation between the Amount of PO_4 adsorbed and the Amount Present in a Bath of Orange II Dye.

TABLE XIII

The Effect of Allowing Aluminum Gel to Adsorb Orange II first then adding Potassium Acid Phosphate to the solution.

PH after dye ads.	PH of final bath	mgm. adsorbed per gm. dry gel			
		Dye ads before salt added.	Dye ads. after salt added.	Dye released.	PO_4 ads.
5.2	4.8	439.4	119.5	373.9	150.7
5.3	4.9	311.1	24.3	286.8	119.1
5.56	5.2	67.0	15.0	52.0	86.9

TABLE XIV

The Effect of Allowing Iron Gel to Adsorb Orange II first, then adding Potassium Acid Phosphate to the solution

PH after dye ads	PH of final bath	mgm. adsorbed per gm. dry gel			
		Dye ads before salt added	Dye ads. after salt added.	Dye released	PO_4 ads.
5.05	4.56	407.6	24.4	383.2	166.0
5.11	5.42	245.7	21.6	224.7	141.0
5.48	5.69	9.7	2.0	7.7	114.4
5.49	5.65	9.7	2.0	7.7	120.0

The data shows that a very high percentage of the dye is displaced by the phosphate. At first thought it would seem that if this were chemical replacement one equivalent of dye should be replaced by one equivalent of phosphate. These values were calculated and not found to agree in any case. This is as it should be for undoubtedly some of the dye was released on dilution of the solution. Or in other words some of the dye compound already formed is dissolved on the addition of the phosphate solution.

The data presented thus far seems to show that the effectiveness of the phosphate in reducing the adsorption of the dye is due to its effect upon the gel. The theory was then advanced that the phosphate covered the exterior surface with an insoluble phosphate and did not leave any ferric hydroxide exposed to react with the acid of the dye. This is in accordance with the theory of Gordon and Marker[4] where they suppose that the dye is adsorbed because of the sodium salt, Orange II, reacting with any acid present to form the acid dye which in turn reacts with the metal hydroxide to form the insoluble metal-dye salt. It is well known that iron and aluminum gels are precipitated in very large particles, and just as the reaction of sulphuric acid on lead is stopped by lead sulfate, here the reaction may be prevented by the formation of iron phosphate on the surface of the gel. If this concept is true we should be able to increase the adsorption of a salt by taking these larger particles of gel and breaking them apart so as to expose new surfaces.

In order to prove this point samples of iron and aluminum gels were allowed to reach a maximum adsorption with potassium acid phosphate. The gel was then removed and ground thoroughly in a mortar for ten minutes; it was then returned to the solution and placed in the mechanical shaker again. Samples were removed, before and after grinding the gel, for analysis. The PH of the solutions was varied by adding potassium hydroxide. 1.05 grams of gel (90% Fe_2O_3 and 74.5% Al_2O_3 respectively) were used with 200 cc of $.05M KH_2PO_4$.

TABLE XV

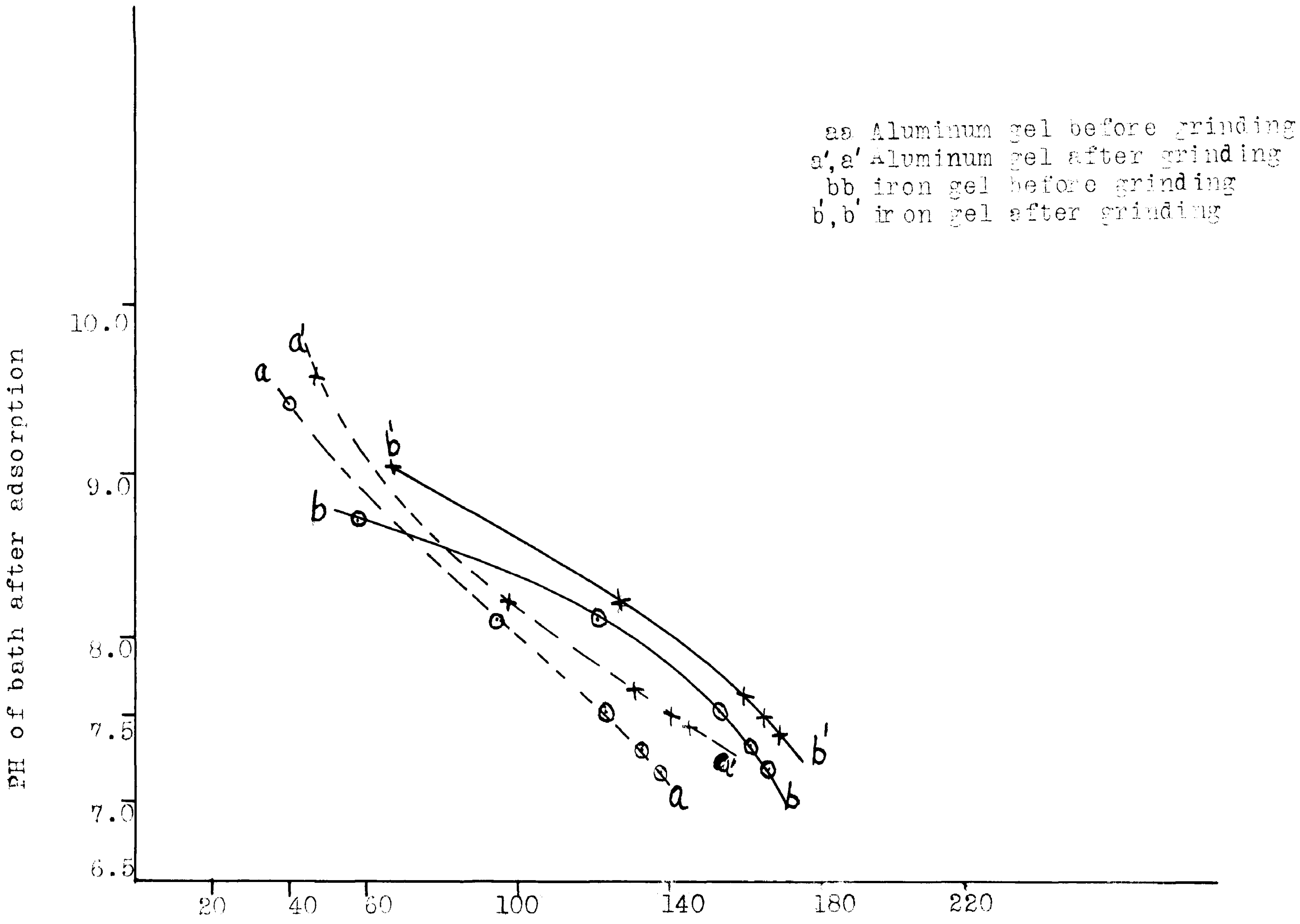
The Effect of Further Subdivision of the Particle of Aluminum Gel.

PH of original salt solutions	PH of bath before grinding	PH after grinding	mgm. PO_4 ads per gm dry gel		
			before grinding	after grinding	increase
4.683	7.168	7.405	138.4	147.7	9.3
5.799	7.328	7.422	135.6	143.3	7.6
6.287	7.532	7.641	127.6	132.5	4.9
7.084	8.081	8.182	94.4	97.1	2.7
10.718	9.417	9.552	41.1	46.4	5.4

TABLE XVI

The Effect of Further Subdivision of the Particle of Iron Gel.

PH of original salt solution	PH of bath before grinding	PH of bath after grinding	mgm. PO ads. per gm dry gel		
			before grinding	after grinding	increase
4.683	7.151	7.354	166.2	171.5	5.3
5.799	7.303	7.439	163.4	166.1	2.7
6.289	7.557	7.624	154.2	160.7	5.5
7.084	8.098	8.149	121.2	126.0	4.8
10.718	8.706	9.028	58.7	68.8	10.1



Graph IV. The Effect of Further Subdivision of the Particles of Gel, on Adsorption of Phosphates.

The difference in PH between the first and second column does not give the PH change corresponding to the phosphate adsorbed because quite a bit of water was added with the gel. In a total of 48.3 grams of gel plus water there was 47.3 grams of water. With the iron gel in the above experiment even after filtering there was considerable colloidal ferric phosphate in the solution. For the phosphate determination this was removed by saturating the solution with ammonium nitrate which precipitated the colloid. On filtering, the solution was perfectly clear.

The data given in the two preceding tables is presented in Graph IV.

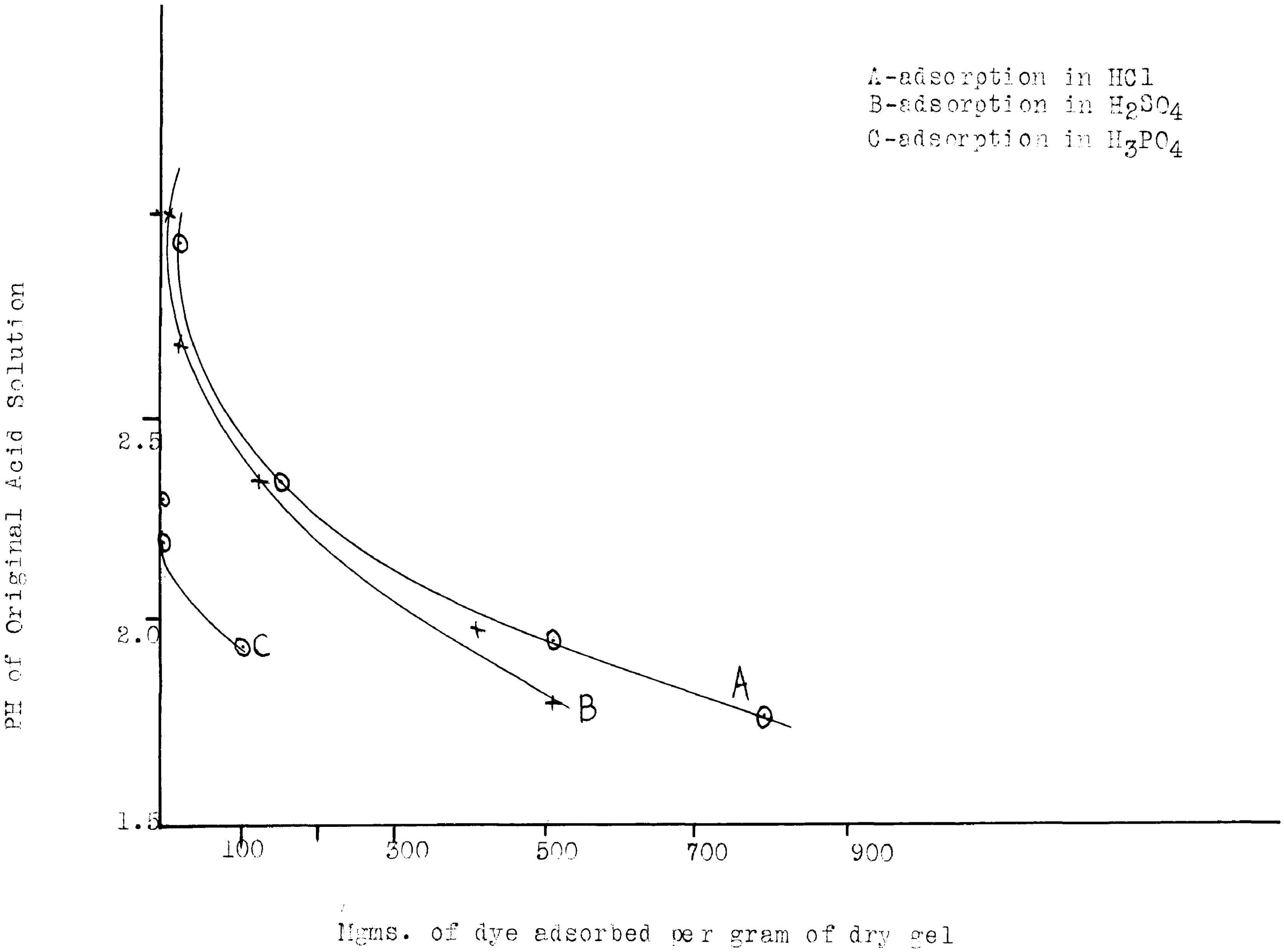
From these curves it is readily seen that there was quite a definite increase in the adsorption of phosphates by both iron and aluminum gels when new surfaces were exposed by crushing the gel particle. This seems to show that the surface of the gel, when maximum adsorption is reached, is coated with a definite film of phosphate which is impervious to more phosphate or dye under the existing conditions. But when one of these phosphate coated particles is broken and a new surface exposed, more of the phosphate can be taken up from the solution. This might appear to be then the explanation of the fact that phosphates cut out the adsorption of an acid dye by iron gel. If the layer of phosphate formed cannot be penetrated by additional phosphate from phosphoric acid, then it is reasonable to suppose that the dye cannot penetrate the film. But in experiments following this where less phosphate was used and was still effective in preventing the adsorption of the dye, it is hardly conceivable that there is a sufficient amount of the phosphate radical present to cover the whole surface of the gel. This data, though, certainly seems to explain the always troubling assertion that there is apparently never a definite chemical equivalent relationship between the amount of material adsorbed and the amount of gel present. All of the preceding data was recalculated on the basis that the dry gel was 74.5% Al_2O_3 and 90% Fe_2O_3 respectively and no definite chemical combining ratios were found between the dye or salt adsorbed and the iron or aluminum present as gels. None should be expected according to the data presented in Tables 15 and 16 because at all times there might be quite a large core of aluminum hydroxide or iron hydroxide within the gel particle that never comes in contact with the solution and hence cannot be acted upon.

In all of the data presented the adsorption of the dye in phosphoric acid has been compared to the adsorption in sulphuric acid. In order to have a comparison of the effects of the ions Cl^-, SO_4^{--}, and PO_4^{---} upon the adsorption of Orange II an experiment was run using hydrochloric, sulphuric and phosphoric acids of the same PH values to dissolve the dye, and iron aluminum and chromium gels as adsorbing mediums. The same amounts of gel and the same percentage dye solution (.5%) were used in each case. The results are given in grams of dye adsorbed per gram of dry gel. The gel in this state in the case of iron is 90% Fe_2O_3, that of aluminum 74.5% Al_2O_3 and chromium 70.4% Cr_2O_3.

TABLE XVII

The Adsorption of Orange II by Iron Gel in the Presence of three different Acids under the same PH.

PH of acid sol. before dye added	mgm. of dye adsorbed per gm. of dry gel		
	HCl	H_2SO_4	H_3PO_4
2.95	8	8	00
2.66	28	15	00
2.33	143	138	00
2.01	440	417	30
1.94	540	500	102



Graph V Adsorption of Orange II by Iron Gel in the Presence of HCl, H_2SO and H_3PO_4

It is shown here that in their adsorption effects with iron gel, HCl and H_2SO_4 are very much alike and H_3PO_4 has cut out the adsorption entirely except at a very low PH. The results with chromium gel are very similar, these are shown in the following table and in Graph VI.

Table XVIII.

The Adsorption of Orange II by Chromium Gel in the Presence of three different acids under the same PH.

PH of acid sol. before dye added	mgm of dye ads. per gm. of dry gel		
	HCl	H_2SO_4	H_3PO_4
2.95	24	24	5
2.66	41	35	4
2.33	155	150	00
2.01	475	346	15
1.94	500	390	88

It is apparant that hydrochloric and sulphuric acids have almost the same effect again except at a very low PH, and phosphoric acid has very greatly reduced the adsorption. The adsorption in the presence of phosphoric acid passes through a minimum. This result is explained in the theory of this reaction which is developed in the latter part of this paper. With Aluminum Gel the results are similar.

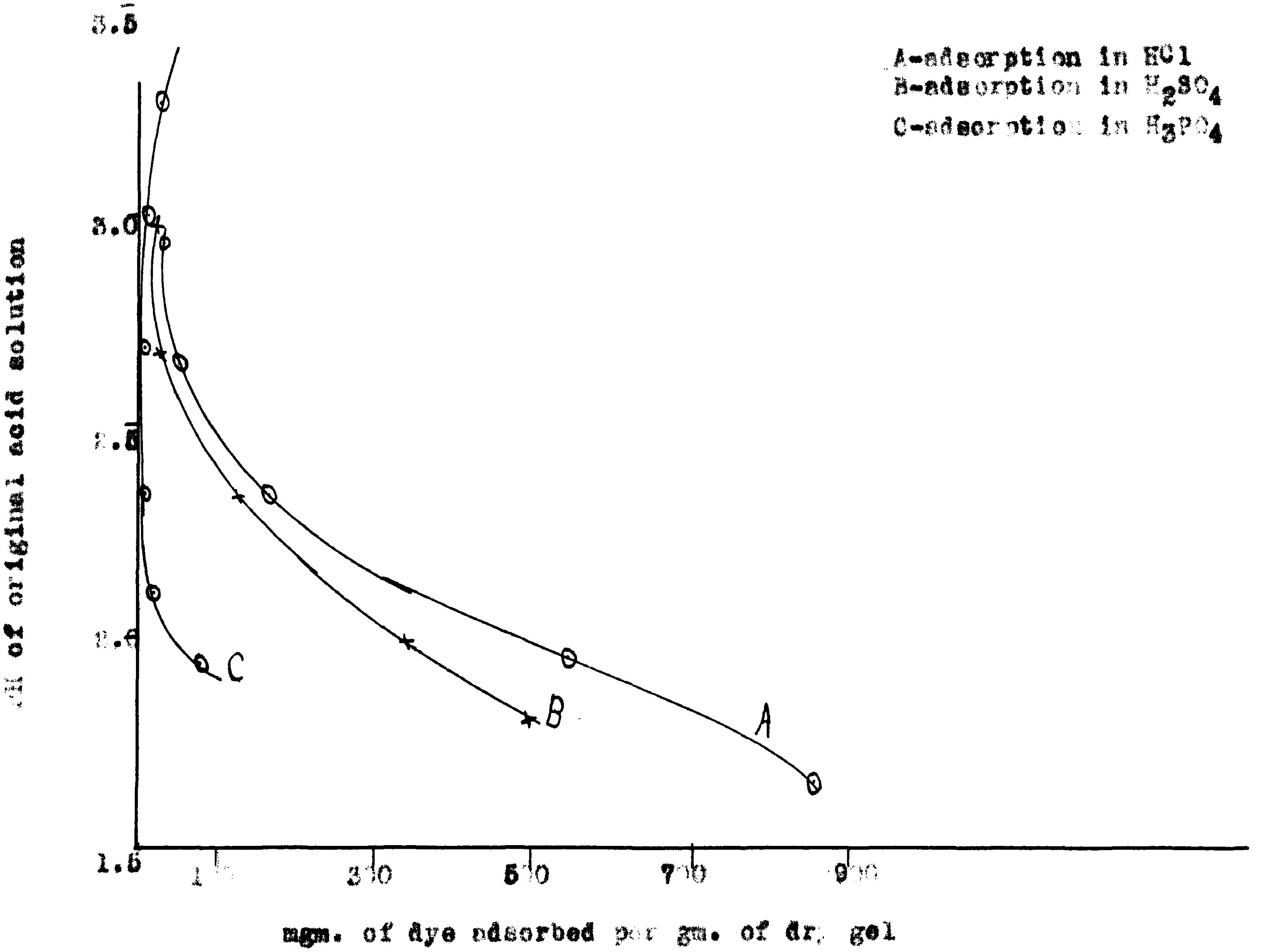
TABLE XIX

The adsorption of Orange II by Aluminum Gel in the presence of three different acids under the same PH.

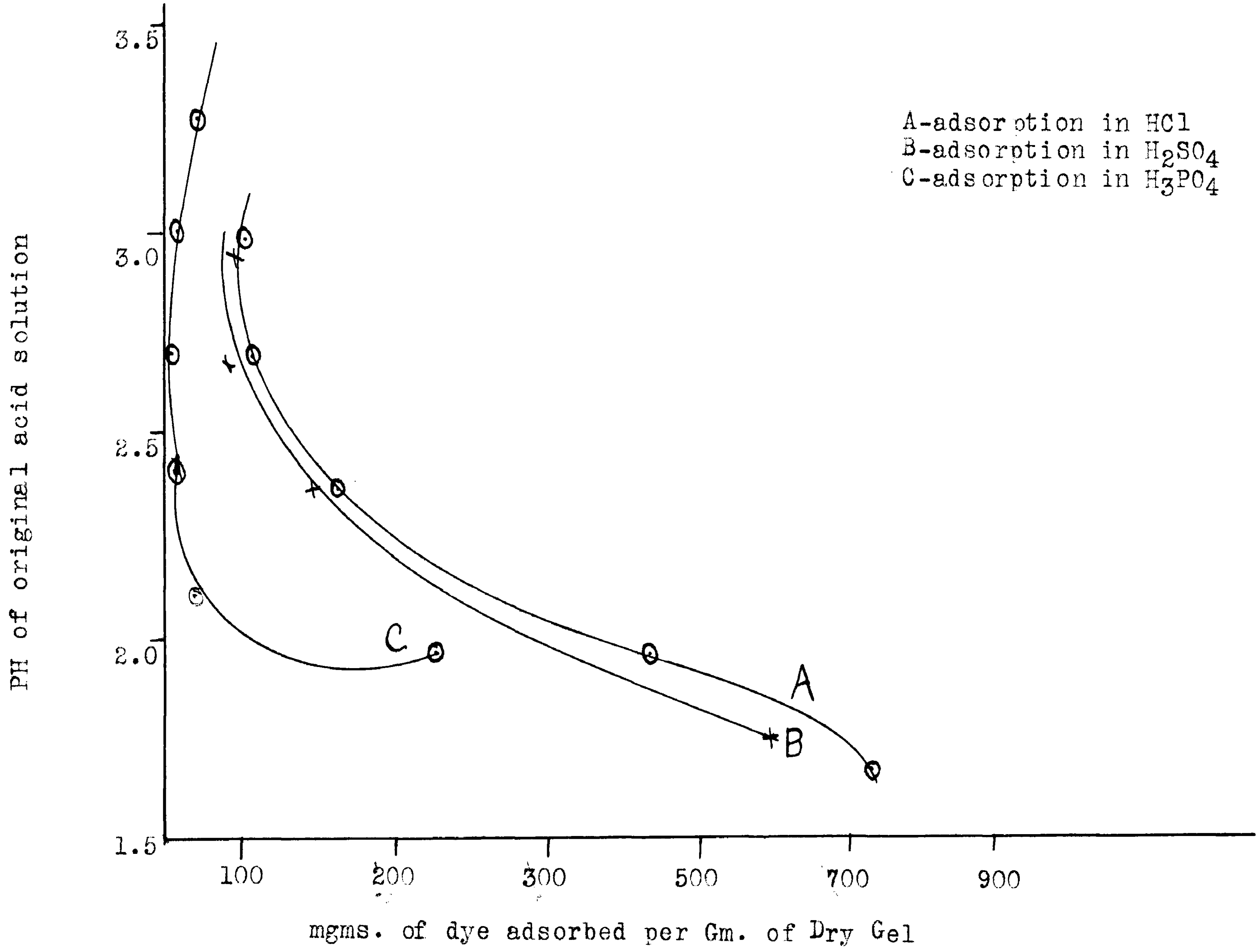
PH of acid sol. before dye added	mgm of dye ads. per gm. of dry gel		
	HCl	H_2SO_4	H_3PO_4
2.95	90	95	15
2.66	95	96	1
2.33	222	215	25
2.01	560	540	160
1.94	650	620	363

These results are brought out more clearly in Graph VII Here again hydrochloric acid seems to offer the best adsorption medium with sulphuric acid very nearly equal to it and with phosphoric acid there is very little adsorption at all. At a very low PH the amount of dye adsorbed with phosphoric acid present increases very rapidly.

Since the control of the PH has been shown to be a very important factor it was carefully followed in all the stages of the above experiment. The results are given sep-



Graph VI Adsorption of Orange II by Chromium Gel in the Presence of HCl, H_2SO_4, and H_3PO_4



Graph VII Adsorption of Orange II by Aluminum Gel in the Presence of HCl, H_2SO_4 and H_3PO_4

arately for each acid.

When the gel was added to the dye solutions it was mixed with a considerable quanitiy of water, (47 gms. water plus 1 gram gel). The dilution and the PH of this water had an effect upon the final PH of the bath, but since this was constant in every case it does not enter into the comparison of the effects of the acids. The water with iron gel had a PH of 7.5, that with aluminum 8.36 and with chromium 8.35.

TABLE XX

The PH changes during the adsorption of Orange II in the presence of HCl

PH of original acid solution before dye added	PH of solution after adding 1 gm of dye to 200 cc sol.	PH of bath after equilibrium was reached.		
		Al gel.	Cr gel.	Fe gel.
2.95	6.4	6.63	6.91	6.74
2.66	6.0	5.85	6.93	6.34
2.33	x	5.48	6.27	6.12
1.96	x	5.24	5.85	5.10
1.65	x	3.82	2.47	----

In the solutions marked x the PH could not be taken due to the dye precipitating out on the eletrode.

TABLE XXI

The PH changes during the adsorption of Orange II in the presence of sulphuric acid

PH of original acid solution before dye added	PH of solution after adding 1 gm dye to 200 cc sol.	PH of bath after equilibrium was reached.		
		Al gel.	Cr gel.	Fe gel.
2.98	6.4	7.12	7.14	6.30
2.69	6.3	6.71	7.13	5.85
2.38	x	6.08	6.40	5.48
2.01	x	—	5.58	4.94
1.79	x	3.82	4.72	—

TABLE XXII

The PH changes during the adsorption of Orange II in the presence of phosphoric acid.

PH of original acid solution before dye added	PH after adding 1 gm. dye to 200 cc solution	PH of adsorption bath after equilibrium was reached		
		Al gel.	Cr gel.	Fe gel.
3.29	6.66	7.40	7.20	6.47
3.01	6.59	7.13	7.10	6.32
2.74	4.9	7.05	7.00	6.28
2.42	x	7.46	6.10	6.20
2.18	x	5.10	5.88	4.81
1.94	x	3.20	2.57	2.08

The increase in PH of the solution on mixing the dye with the acid is due to the neutralization of the acid by the hydrolysis of the dye which is the salt of a strong base and a weak acid. The reaction thus forms the acid of the dye and the sodium salt of the acid radical. It was the formation of this dye acid that made it impossible to determine the PH of the solutions marked x, for when this material is present in large quantities it precipitates on the electrode.

It will be noticed in the above data that when the final PH of the bath was in general below 6.5 with hydrochloric and sulphuric acids quite a large amount of dye was adsorbed. This point varies, of course, with the different gels. But with phosphoric acid before any quantity of adsorption could be obtained the final PH of the bath was lowered to 3.2 for aluminum gel, 2.57 for chromium gel and 2.07 for iron gel.

A few drops of chromium, aluminum, and ferric chlorides were added to the respective phosphoric acid dye baths which had given little or no adsorption. A precipitate of the metal dye compound immediately resulted. This seemed to indicate that one of the conditions necessary to get the dye removed or adsorbed was to have the metal present in an ionizable compound. Had the ions been present before, adsorption would have resulted. At almost any PH value when sulphuric or hydrochloric acid is in the presence of aluminum, iron, or chromium gel, metallic ions will be liberated because of the formation of a soluble sulfate or chloride. With phosphoric acid reacting with the gel, aluminum, iron or chromium phosphate would form, all of which are relatively insoluble except in more concentrated acid solutions. If this theory is true that the liberation of the metallic ion is necessary in order for it to react with the dye and form the metal-dye compound, then we should find, at the PH values where adsorption was obtained with phosphoric acid, that iron phosphate is soluble and will yield ferric ions in solution. In order to determine this the following experiment was preformed.

Ferric phosphate was prepared by treating potassium dihydrogen phosphate with ferric chloride. A white flocculent precipitate was obtained which became curdy on boiling. To equal amounts of this were added varying amounts of .2N phosphoric acid. This was boiled and let stand for a few hours. In some of the tubes it could be seen that some of the ferric phosphate had dissolved, but some white precipitate still remained in all of them. The PH values of the solutions were determined and they were tested for ferric ions with potassium sulfo-cyanide. At a PH of 6.88 no ferric ions were present. At 2.40 there was a faint test for ferric ions lower than this at PH 2.077 and 2.029 the number of ions in solution increased greatly. This can be tested qualitatively by adding KCNS to ferric chloride and then adding Na_2HPO_4 the color will disappear now if phosphoric acid is added, the characteristic red color of ferric ions will reappear due to the ferric phosphate formed dissolving again.

In order to confirm this and have conditions exactly the same as in the dye adsorption experiment, iron gel was mixed with phosphoric acid solutions of various concentrations and subjected to the same conditions which the adsorption of the dye was carried out. Results were obtained confirming those given above. With solutions of PH above 4.00 no ferric ions were found in solution. Below this the lower the PH the more ions there were present.

Aluminum phosphate was prepared by treating a solution of potassium monohydrogen phosphate with aluminum chloride. This was treated in the same manner as the iron. A total of seven solutions were used. In these the number of aluminum ions present seemed to pass through a minimum at PH of 5.6 above this number of ions present increased and below this the lower the PH the greater was the number of ions present. It is believed that this is due to the ampotheric nature of the aluminum. Referring back to Table 19 and Table 22 we find that the amount of Orange II adsorbed passes through a minumum when the final PH of the bath corresponds very closely to this.

Chromium phosphate was prepared in exactly the same manner as iron phosphate and a similar experiment tried. At a PH of 6.0 there was a trace of chromium ions in solution but they did not appear in an appreciable amount until a PH of 2.8 was reached, lower than this the amount present increased rapidly. Referring back to Tables 18 and 22, it will be noticed that with chromium gel a small amount of dye was adsorbed in the presence of phosphoric acid at a PH of 5.6 but the first adsorption of a large amount of dye was at a PH of 2.6.

In every case the adsorption of the dye checks very closely with the amount of metal passing into solution in the form of ions. Here we believe is the explanation of the effect of the phosphate radical on the adsorption of an acid dye. The amount of dye removed depends upon the number of metal-ions there are in solution to react and form the metal-dye compound. Hydrochloric and sulphuric acids react with the gels, form soluble salts and furnish the metal ions to the solution. The more acid there is present the more metal ions there will be in solution hence we find the greater adsorption of the dye at the lower PH. With phosphoric acid, however, reacting with the gel relatively insoluble salts are formed and no ions are furnished to the solution until the acidity is of such concentration that it dissolves these salts. As was shown the solubility of these phosphates vary, iron being the most insoluble.

The series of reactions through which this process of dyeing the mordant, goes are thought to be as follows: For simplicity let x represent the dye radical. Gordon and Marker[4] have shown that the compound formed by the dye with the metals is AlX_3, FeX_3 and CrX_3. Aluminum gel and hydrochloric acid are used as an illustration.

NaX plus $HCl \rightleftarrows NaCl$ plus HX ------(1)

That this reaction takes place and forms the weaker acid HX is shown by the great increase in PH when Orange II is added to an acid solution. Data illustrating this are given in Tables 20,21,and 22.

$3HCl$ plus $Al(OH)_3 \rightleftarrows AlCl_3$ plus H_2O ------ (2)

This reaction was proven by taking various mixtures of the acid and gel and testing for the ions formed.

$AlCl_3$ plus $3NaX \rightleftarrows AlX_3$ plus $3NaCl$ ---(3)

The salt AlX_3 is relatively insoluble and is thus removed from the field of action. This reaction has been illustrated by crystals of aluminum, iron, and chromium chloride into a water solution of Orange II. In every casean immediate precipitate results. It is believed that most of the metal-dye compound is formed by this reaction.

Some little may be formed by the reaction of the dye acid and the gel but this is highly improbable since the base is extremely weak and the acid is relatively weak.

$$Al(OH)_3 \text{ plus } 3HX \rightleftarrows AlX_3 \text{ plus } 3H_2O \text{ ----(4)}$$

If this is the essential reaction then phosphoric acid should assist the dying just as effectively as sulphuric or hydrochloric acids, because with phosphoric acid the dye acid HX is formed just as in the other two cases as the data in Table 22 shows.

If no acid is present some small amount of the metal dye salt may be formed due to the slight ionization of aluminum hydroxide.

$$Al(OH)_3 \text{ plus } 3NaX \rightleftarrows AlX_3 \text{ plus } NaOH \text{ ---------(5)}$$

There is also the possibility that some of the dye acid formed reacts with the $AlCl_3$ formed by reaction (2).

$$AlCl_3 \text{ plus } 3HX \rightleftarrows AlX_3 \text{ plus } 3HCl$$

However the evidence seems to indicate that the essential reaction for the formation of the metal-dye compound is reaction (3). On the basis of this we can explain the very sudden increases in adsorption of Orange II at a low PH which were noted by Gordon and Marker[4]. They found that the adsorption of Orange II increased steadily until a certain relatively low PH was reached; at this point further addition of acid caused very rapid increase in the adsorption. We explain this point by claiming that it occurs at the hydrogen ion concentration where enough acid has been added to shift reaction (1) as far as possible to the right. Any more acid added would react directly with the gel and procede through reactions (2) and (3).

With sulphuric acid the reactions given above would be of the same nature as with hydrochloric acid.

With phosphoric acid, reaction (1) is the same as with hydrochloric. But in reaction (2) there would be formed either $Al(H_2PO_4)_3$, $Al_2(HPO_4)_3$ or $AlPO_4$. Since there is a large amount of gel present and only a small amount of acid it is believed that the major compound would be $AlPO_4$. This compound was shown to be relatively insoluble and corresponding salts of chromium and iron still more insoluble. The formation of this insoluble product in reaction (2) would prevent reaction (3) from taking place and hence would prevent adsorption, by this reaction taking place. This is bourn out by the experimental data given above. Aluminum Phosphate was found to be slightly soluble under all the conditions used and some adsorption of the dye was found in all cases. The PH values at which chromium gel gave adsorption of dye in the presence of phosphate were found to correspond with those at which chromium phosphate yielded chromium ions to the solution. And finally, it was found that iron gel in the presence of phosphates adsorbed dye at only a very low PH value, this corresponded to the point at which iron phosphate yielded ferric ions to the solution.

The experimental facts seem to indicate that in order to have an acid dye removed from solution by a gel, in any large quantity, the metal ion must be in solution. This is accomplished by adding sulphuric or hydrochloric acids which react with the gels to form soluble salts. Phosphates decrease the adsorption because of the formation of difficultly soluble salts with the gels.

SUMMARY OF EXPERIMENTAL RESULTS.

I. The presence of .05 normal potassium dihydrogen phosphate greatly decreased the adsorption of an acid dye with Aluminum gel and Iron gel.

II. Using H_3PO_4 solution in the dye bath the adsorption of Orange II was very much decreased with aluminum gel and cut out entirely with iron gel except at a very low PH.

III. Iron gel was allowed to adsorb all of the phosphate from $.01N KH_2PO_4$ and $.01N H_3PO_4$, then Orange

II dye was added. No dye was adsorbed.

IV. Iron and Aluminum Gels were allowed to adsorb dye from a .5% solution of Orange II at PH values varied with KOH and H_2SO_4. Potassium acid phosphate was then added. Most of the dye was released and the phosphate adsorbed.

V. Iron gel was allowed to remain with dye solutions in .05N potassium acid phosphate for a period of six months. Even at the end of this period no dye was adsorbed.

VI. Iron and aluminum gels were allowed to reach adsorption equilibrium with .05N KH_2PO_4. The gels were removed, and ground in a mortar then put back into the solutions. There was an increase in adsorption in all solutions used.

VII. The adsorption of Orange II by iron, aluminum, and chromium gels was tried with the following results.

Aluminum gel: High adsorption of dye with HCl and H_2SO_4.
Low adsorption of dye with H_3PO_4.

Chromium gel: High adsorption of dye with HCl and H_2SO_4.
Very low adsorption of dye with H_3PO_4.

Iron gel: High adsorption of dye with HCl and H_2SO_4.

No adsorption of dye with H_3PO_4 except at a very low PH value.

The order of increasing adsorptive power for Orange II is : iron, chromium, aluminum.

VIII. In cases where phosphate is adsorbed from solutions having varying phosphate concentrations the amount adsorbed in the presence of Orange II dye is a straight line function of the amount present.

IX.Chromium, iron, and aluminum as chlorides when mixed with solutions of the sodium salt of Orange II give an immediate precipitate of the respective metal-dye compound.

X. Chromium, iron, and aluminum chlorides dropped into the H_3PO_4 solution from which no dye was adsorbed gave immediate precipitates of the metal-dye compound.

XI. The solubility of aluminum phosphate in phosphate solutions of various hydrogen ion concentrations was found to coincide with the adsorption cure of Orange II by aluminum gel in phosphate solutions.

Iron phosphate was found to be soluble at the same PH at which the iron gel adsorbed Orange II.

Chromium phosphate was also found to be soluble in phosphate solutions at the same PH where adsorption of Orange II was found.

CONCLUSIONS.

The decrease in the adsorption of an acid dye, Orange II, in iron, aluminum and chromium gels (mordants) by phosphates is not due to any effect of the phosphate radical upon the dye or the solution. It is due to the phosphate forming a relatively insoluble compound with the gels, hence not furnishing any metal ions to react with the dye and form the metal-dye compound which is the cause of adsorption. At high hydrogen ion concentrations adsorption takes place because the metal phosphate becomes soluble. The reactions supposed to take place during the adsorption of an acid dye Orange II by an inorganic gel are best expressed in the following equations:

Let x represent the dye radical and using iron gel with a hydrochloric acid solution of the dye for an example:

NaX plus $HCl \rightleftharpoons NaCl$ plus HX --------(1)
$3HCl$ plus $Fe(OH)_3 \rightleftharpoons FeCl_3$ plus $3H_2O$ --------(2)
$FeCl_3$ plus $3NaX \rightleftharpoons FeX_3$ plus $3NaCl$ --------(3)
$3HX$ plus $Fe(OH)_3 \rightleftharpoons FeX_3$ plus $3H_2O$ --------(4)
$3NaX$ plus $Fe(OH)_3 \rightleftharpoons FeX_3$ plus $3NaOH$ --------(5)

It is postulated that most of the adsorption is due to reaction (3). Some little may be due to reactions (4) and (5).

Sulphuric acid acts very similar to hydrochloric in these reactions.

Phosphoric acid acts in reaction (1) similar to hydrochloric. In reaction (2) phosphoric acid forms an insoluble iron phosphate thus preventing reaction(3) from taking place and no adsorption results unless the solution is made sufficiently acid to dissolve the iron phosphate.

Aluminum and chromium gels act similar to iron.

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