[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WASHINGTON]

The Influence of Adsorbed Ions on the Dissolution of Colloidal Aluminum Hydroxide in Hydrochloric Acid

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In a previous research in this Laboratory[1] it was found that when colloidal aluminum hydroxide was peptized with hydrochloric acid, the hydrogen-ion concentration of the resulting sol gradually changed with time. For example, a sol consisting of aluminum hydroxide peptized with hydrochloric acid had an initial *P*H of 2.30 which gradually changed to *P*H 3.89 a year later. Even after this lapse of time, equilibrium had not been reached. These results indicated that hydrochloric acid reacts very slowly with colloidal aluminum hydroxide, which is free from other electrolytes. It is well known, however, that aluminum hydroxide reacts readily with hydrochloric acid in the presence of other electrolytes, as is evidenced by the usual procedures for the separation and estimation of aluminum in qualitative and quantitative analysis.

In this paper data are submitted on the effect of the presence of certain anions, phosphate, sulfate and arsenate, on the speed of the reaction between colloidal aluminum hydroxide and hydrochloric acid. The experimental evidence obtained is not in agreement with existing theories[2] concerning reactions in heterogeneous systems and shows that the arrangement and spacing of ions and the electrical potential difference at the interface between the phases may have a dominant influence on the speed of reaction.

Experimental

Preparation of Colloidal Aluminum Hydroxide.—One hundred twenty-five grams of carefully purified aluminum chloride was dissolved in two liters of distilled water. The aluminum hydroxide was precipitated by quickly mixing this solution with two normal ammonium hydroxide in quantity sufficient to assure a slight excess of the amount needed for complete precipitation. The material was very energetically stirred during the mixing and then divided equally between three six-liter Pyrex flasks and distilled water added to bring the total volume of each to about five liters.

The precipitated aluminum hydroxide was then washed free of chloride ion according to the method used by Tartar and Damerell.[3] A sample of the colloid, when dissolved in nitric acid, showed no turbidity with silver nitrate. The contents of the three flasks were then combined and made up to the desired volume.

For all determinations, samples of the aluminum hydroxide were taken while the colloid was being stirred vigorously by an electrically driven stirrer especially

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(1) Damerell and Tartar, *J. Phys. Chem.*, **36**, 1419 (1932).

(2) Noyes and Whitney, *Z. physik. Chem.*, **33**, 679 (1900); Nernst and Brunner, *ibid.*, **63**, 52 and 56 (1904); Senter, *ibid.*, **51**, 696 (1905); Teletew, Dissertation, Heidelberg (1906); Jablczinsky, *Z. physik. Chem.*, **64**, 748 (1908); Spear, THIS JOURNAL, **30**, 195 (1908); Bodenstein, *Z. physik. Chem.*, **60**, 1 (1907); Schleudenberg, *J. Phys. Chem.*, **12**, 583 (1908); Van Name, *Am. J. Sci.*, **29**, 237 (1910); **32**, 207 (1911); **36**, 543 (1913); **42**, 301 (1916); **43**, 449 (1917); Erickson-Auren and Palmaer, *Z. physik. Chem.*, **61**, 689 (1906); Marc, *ibid.*, **61**, 385 (1908); Wildermann, *ibid.*, **66**, 445 (1909).

(3) Damerell and Tartar, *J. Phys. Chem.*, **36**, 1419 (1932).

designed for the purpose. The same 25-ml. pipet was used for taking samples during this entire research. The samples contained 0.1507 ± 0.0018 g. of aluminum hydroxide.

Preparation and Standardization of Reagents.—The phosphate salt used was disodium hydrogen phosphate, Na_2HPO_4. A solution was made and standardized by determining the phosphate content by precipitation as magnesium ammonium phosphate, ignition and weighing as magnesium pyrophosphate. From this solution, two solutions of convenient concentration were prepared, 0.05 molar and 0.005 molar.

The potassium sulfate solution used was prepared from an analyzed sample, which was recrystallized and then dried for five days at 150°. The solution of potassium hydrogen sulfate, $KHSO_4$, was made up from salt which had been purified, recrystallized, and dried for five days at 110°.

The arsenate was recrystallized disodium hydrogen arsenate, $Na_2HASO_4 \cdot 7H_2O$. On account of the uncertainty of the amount of water of hydration a solution of approximately the desired concentration was prepared which was then standardized by reduction to arsenite and titration with standard iodine solution.

Methods of Analysis.—Three methods of analysis for aluminum were used in this research: one for aluminum in the presence of phosphate, another in the presence of sulfate or no interfering anion, and the last in the presence of arsenates.

For aluminum in the presence of phosphates the method of Hillebrand and Lundell was used.[4] The sulfate ion does not interfere with the precipitation of aluminum hydroxide. This determination was also carried out according to the directions given by Hillebrand and Lundell.[5]

Aluminum arsenate is precipitated in alkaline solution. Therefore, the arsenic must be removed before the aluminum is precipitated as the hydroxide. To accomplish this, the samples in which arsenic was present were diluted to 200 ml., made three normal in hydrochloric acid, saturated with hydrogen sulfide and kept under this gas at the pressure of a Kipp generator overnight. The samples were then filtered and the arsenic sulfide precipitate washed with dilute hydrochloric acid saturated with hydrogen sulfide. The arsenic sulfide precipitates were dissolved in ammonia and reprecipitated to make certain that no aluminum was lost by occlusion or adsorption by the arsenic sulfide. The filtrates of each sample were combined, evaporated to 200 ml., again saturated with hydrogen sulfide to assure complete reduction and precipitation of the arsenate. The aluminum was then determined as in the presence of sulfate.

Method of Procedure and Experimental Results.—To determine the effect of a given anion upon the solubility of aged colloidal aluminum hydroxide in hydrochloric acid, 25-ml. portions of well mixed colloid were pipetted into 125-ml. bottles, distilled water added in sufficient quantity to give the whole a final volume of 100 ml., varying amounts of anion added, and finally enough hydrochloric acid to make its concentration 0.2 normal except when disodium hydrogen arsenate was used (see later part of this paper). The bottles were then placed on a shaker submerged in a thermostat held at 25 ± 0.02°. After a reaction period of exactly twenty-four hours the samples were centrifuged at 2500 r. p. m. in an International Centrifuge No. 1. Complete settling was obtained in all cases except those with no or very small amounts of phosphate. Fifty-ml. aliquots were pipetted from each bottle and analyzed for aluminum content as described above.

Runs were made using both sodium sulfate and sodium hydrogen sulfate. With the former salt there is a considerable lowering of hydrogen-ion concentration when it is added to 0.2 *N* hydrochloric acid. The ionization of the HSO_4^- ion is relatively

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(4) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, p. 399.

(5) Hillebrand and Lundell, *ibid.*, p. 397.

small and there is less buffering effect when potassium hydrogen sulfate is added to the hydrochloric acid. For this reason the runs made with this salt are more nearly comparable with respect to hydrogen-ion concentration.

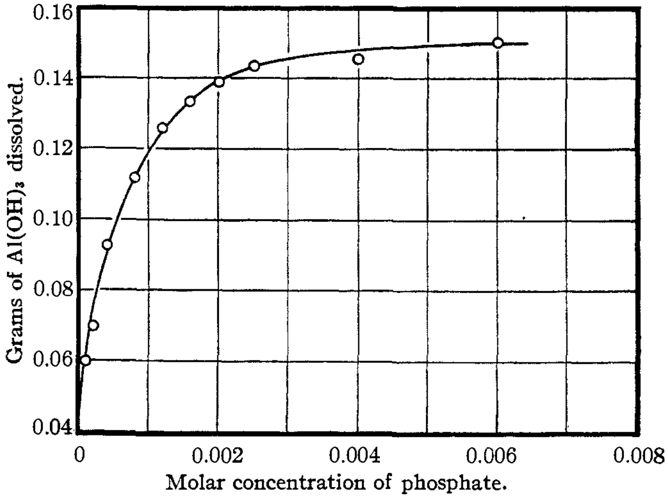


Fig. 1.—Influence of phosphate on dissolution of aluminum hydroxide.

Solutions of disodium hydrogen arsenate are distinctly alkaline and sufficient hydrochloric acid was added to make the initial hydrogen-ion activity the same as that of 0.2 N hydrochloric acid as shown by colorimetric comparisons using thymol blue indicator.

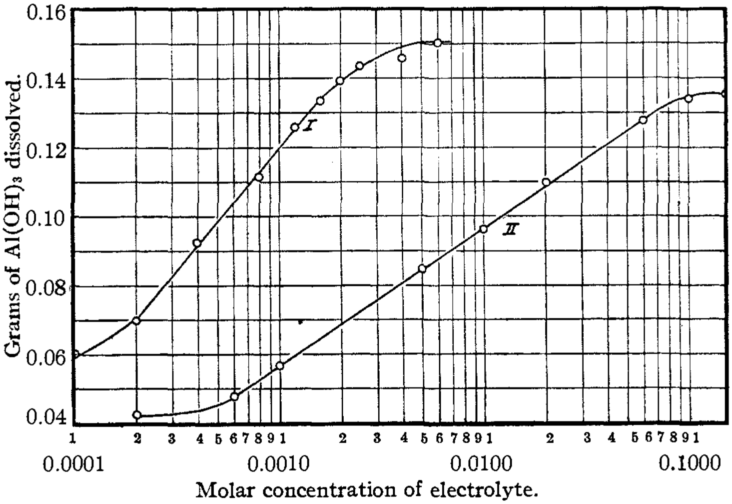


Fig. 2.—Influence of phosphate and arsenate on dissolution of aluminum hydroxide: Curve I, phosphate; Curve II, arsenate.

The runs using no or very small concentrations of phosphate, sulfate or arsenate gave slightly turbid solutions at the end of the centrifuging. A correction for this turbidity was made by comparison with very dilute sols of aluminum hydroxide of known concentration.

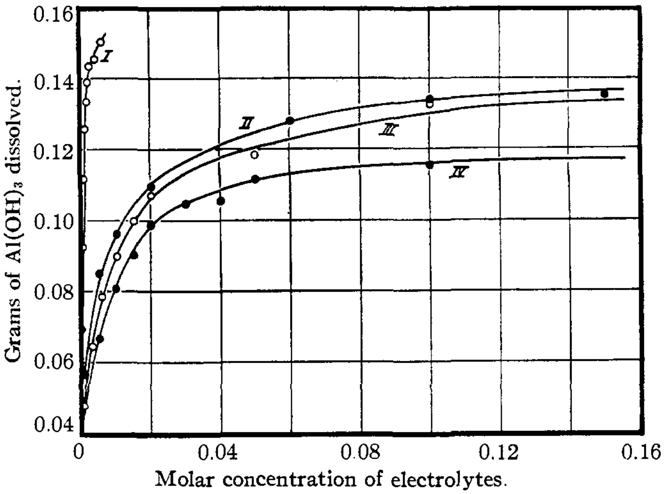


Fig. 3.—Influence of phosphate, Curve I; of arsenate, Curve II; of potassium hydrogen sulfate, Curve III; and of potassium sulfate, Curve IV.

Figures 1 and 2 present the results on the effect of phosphate on the rate of solution of aluminum hydroxide in 0.2 *N* hydrochloric acid. Figures 3 and 4 give the effect

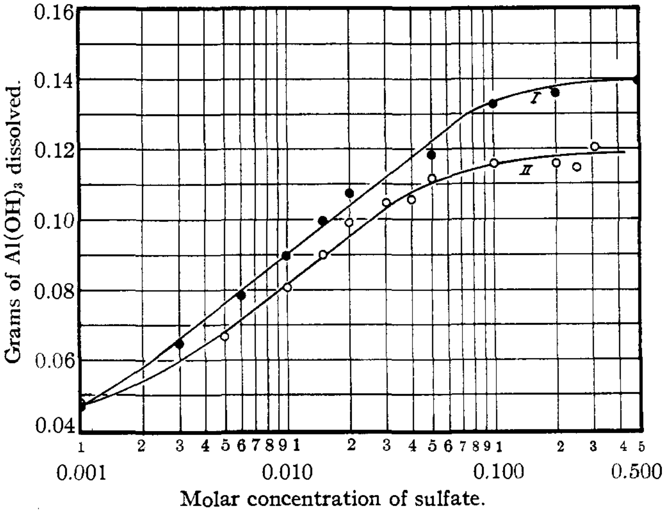


Fig. 4.—Influence of potassium hydrogen sulfate, Curve I; and of potassium sulfate, Curve II.

of potassium sulfate; Figs. 3 and 4, the effect of potassium hydrogen sulfate, and Figs. 2 and 3 the results obtained with disodium hydrogen arsenate.

Discussion of Results

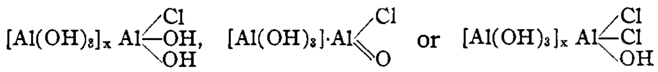
The results show that the speed of the reaction between colloidal aluminum hydroxide and 0.2 N hydrochloric acid is increased several fold by the presence of electrolytes yielding anions of higher valence. Practically complete dissolution of the aluminum hydroxide in twenty-four hours was obtained when the concentration of the phosphate was only 0.006 molar. During the same time, arsenate 0.1 molar produced solution of 89% of the colloid, while sulfate 0.1 molar gave 86%. With the 0.2 N hydrochloric acid alone only 26.5% of the colloid reacted.

Within certain limits, the amount of aluminum hydroxide reacting during the twenty-four hour period can be expressed in the form of equations derived from Figs. 2 and 4 showing that the amount dissolved is a logarithmic function of the concentration of phosphate, sulfate or arsenate. The equations take the general form

$$\chi = K \log a + C$$

where χ represents the amount of aluminum hydroxide dissolved in twenty-four hours, a the molar concentration of the electrolyte furnishing bivalent or trivalent anions, t the time and K and C are constants, the values of which depend primarily upon the nature and concentration of the electrolyte, area of interfacial surface, hydrogen-ion activity and temperature. For example, the equation for the phosphate series is: $\chi = 0.07 \log a + 0.33$. These equations do not apply with very small concentrations of these salts nor when most of the colloidal material has been dissolved. This point will receive comment in a later part of this paper.

The writers believe that the experimental results presented herein can be best explained as being due to the anions of higher valence modifying the speed of the reactions by their influence on the electrical potential difference at the solid–liquid interface. The positive charge on the colloidal particles of aluminum hydroxide is commonly attributed to the preferential adsorption of hydrogen ion from the water or acid or to the ionization of colloidal particles of the type



$$[\mathrm{Al(OH)_3}]_x\,\mathrm{Al}\begin{matrix}\diagup\mathrm{Cl}\\ -\mathrm{OH},\\ \diagdown\mathrm{OH}\end{matrix}\quad [\mathrm{Al(OH)_3}]\cdot\mathrm{Al}\begin{matrix}\diagup\mathrm{Cl}\\ \diagdown\mathrm{O}\end{matrix}\quad \text{or}\quad [\mathrm{Al(OH)_3}]_x\,\mathrm{Al}\begin{matrix}\diagup\mathrm{Cl}\\ -\mathrm{Cl}\\ \diagdown\mathrm{OH}\end{matrix}$$

In any case, the positively charged surface is accompanied by a layer of negatively charged chloride ions near the interface. There is, therefore, an arrangement and spacing of ions at the interface which produces an electrical potential difference (p. d.). According to the conception of Gouy and of Debye and Hückel,[6] there is a potential gradient outward from the solid surface due to the relative proportion of negative to positive ions, which steadily decreases until the concentrations of both kinds of ions be-

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(6) Gouy, *J. phys. chim.*, [4] **9**, 457 (1910); Debye and Hückel, *Physik. Z.*, **24**, 185 (1923); La Mer, *Trans. Am. Electrochem. Soc.*, **51**, 528 (1927).

come the same as that in the bulk of the solution. This arrangement of the ions permits the reaction with the acid to take place slowly, probably only for brief lengths of time at certain spots on the surface of the colloid.

The data from the experiments show the dominating influence of the valency of the anion. Both phosphoric acid and arsenic acid are more effective than sulfuric acid; phosphoric acid shows its marked effects at very low concentrations. A comparison of the data on the arsenate and the sulfate shows that an extremely small quantity of the trivalent arsenate ion is more influential than the comparatively large concentration of the bivalent sulfate ion. Work in this Laboratory has shown that both the phosphate and the arsenate are highly adsorbed by the colloidal aluminum hydroxide.

At very low concentrations of the added electrolyte, the semi-logarithmic curves break from a straight line and show results somewhat high compared with the main part of the curve. This would seem to indicate that the first portions of the bivalent or trivalent anions adsorbed exert a greater influence on the speed of the reaction. The authors are inclined, however, to the opinion that this deviation of the curve is due to the presence of small amounts of impurities which accelerate the reaction such as dissolved carbon dioxide and possibly substances dissolved from the walls of the glass containers.

At the other end of the semi-logarithmic curves there is another bend showing that the speed of the reaction is not so markedly increased. This gradual change is undoubtedly due to the decrease both in surface and hydrogen-ion concentration.

The fact that a change of approximately 14% of the hydrogen-ion activity had no discernible effect on the rate of solution demonstrates clearly that the rate of diffusion is not the important factor. The addition of phosphate equivalent to 0.0004 molar, which produced a calculated concentration of 7.75×10^{-21} of phosphate ion, which is a molar concentration equivalent to $5 \times 10^{-18}\%$ of the hydrogen-ion activity, or if in the form of the $HPO_4^{=}$ ion an addition 3.33×10^{-9} molar and equivalent to $2.15 \times 10^{-6}\%$, produces an increase in the speed of the reaction of 230%.

The lower values with potassium sulfate than with potassium hydrogen sulfate are due to the large buffering effect of the former, which lowered the hydrogen-ion concentration of the solution.

The change in the speed of the reaction is not from an increase in the surface of the colloid due to peptization by the added electrolyte. In fact, the reverse is true; the phosphate, arsenate and sulfate exert flocculating effects with probably some decrease in the interfacial surface. These were more readily clarified by centrifuging at the end of the reaction period, thus affording experimental evidence that the particles were of larger size.

Summary

1. Data on the influence of phosphates, sulfates and arsenates on the dissolution of aged colloidal aluminum hydroxide in 0.2 N hydrochloric acid, have been presented.

2. Within certain limits, the amount of the hydroxide dissolved is a logarithmic function of the concentration of the electrolyte yielding bivalent and trivalent anions. The equations take the form $\chi = K \log a + C$.

3. The influence of the anion of higher valence is attributed to adsorption at the solid-liquid interface which produces a reduction in the electrical potential difference.

4. The findings are not in accord with the diffusion theory of reactions in heterogeneous systems.

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Relative Strength of Benzoic and Salicylic Acids in Alcohol-Water Solutions

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An earlier paper[1] presented measurements of the relative strength of a series of carboxylic acids in 50% ethyl alcohol and 60% butyl carbitol, determined by means of the antimony electrode. In those measurements, as in others,[2] the presence of a liquid junction between solutions in different solvents might be used as a basis for adverse criticism. It is therefore desirable to compare the results of a similar set of measurements with those obtained by an independent method. For this purpose the relative strength of benzoic and salicylic acids in a series of ethyl alcohol-water solutions has been determined with the antimony electrode and from the solubilities of the acids and their silver salts. The agreement justifies the assumptions of both procedures, and suggests that the earlier measurements in 50% alcohol, and, by inference, in 60% butyl carbitol, are more accurate than was originally claimed.

This result has an important bearing on the question of the variation of the relative strength of acids in different solvents. It seems reasonable, *a priori*, to assume that the relative ionization, in conformity with equilibria in general, should be conditioned by the solvent as well as by the acids. However, since the data which support this view were obtained exclusively by the use of cells with questionable liquid junctions, it could not be

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(1) Halford, THIS JOURNAL, **53**, 2944 (1931).

(2) Conant and Werner, *ibid.*, **52**, 4436 (1930); Hall, *Chem. Rev.*, **8**, 191 (1931); Michaelis and Mizutani, *Z. physik. Chem.*, **116**, 135, 350 (1925).