[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF GEORGIA]

The Similarity of Aluminum Salt Solutions and Aluminum Hydrosols

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Introduction

In a previous paper[1] one of the authors pointed out the apparent similarity of aluminum and chromium salt solutions and suggested that aluminum hydrosols might be large aggregates of basic aluminum salts. Thomas and von Wicklen[2] working with chromium hydrosols compared their results with those of Thomas and Whitehead[1] and found them similar. Thomas and von Wicklen postulated a Werner type formula for their chromium hydrosols, assuming them to be made up of large aggregates of basic chromium salts.

Previous investigators[3] have reported many isolated peculiarities of aluminum salt solutions but offered no explanations for them. However, basic chromium salt solutions have been more thoroughly studied, particularly by Stiasny, Bjerrum and Gustavson.[4]

This paper is another attempt to compare experimentally, under controlled conditions, aluminum salt solutions, basic aluminum salt solutions and aluminum hydrosols.

Experimental

Solutions of $AlCl_3$, $Al(OH)Cl_2$, $Al(OH)_2Cl$ and aluminum oxychloride hydrosol all of the same aluminum content were prepared. The $Al(OH)Cl_2$, and $Al(OH)_2Cl$ solutions were prepared by adding one-third and two-thirds, respectively, of the stoichiometric quantities of sodium hydroxide necessary to titrate the aluminum chloride solution potentiometrically. The $AlCl_3$, $Al(OH)Cl_2$, $Al(OH)_2Cl$ solutions were then diluted with the necessary amounts of distilled water to bring them to equivalent concentrations with respect to aluminum content. They were allowed to stand until they were no longer turbid. The aluminum oxychloride hydrosol was prepared according to the method given by Whitehead.[5]

Solutions of the anions were prepared by weighing out equivalent amounts of their salts and dissolving them in a liter of distilled water. They were made up one normal in strength so that more dilute solutions could be made from them and keep the total volume constant.

TABLE I

*P*H VALUES OF ALUMINUM SALT SOLUTIONS AND HYDROSOL AT 25°

Material	$AlCl_3$	$Al(OH)Cl_2$	$Al(OH)_2Cl$	Hydrosol
*P*H	4.03	4.10	4.30	4.00

TABLE II

*P*H VALUES OF 0.5 NORMAL SALT SOLUTIONS AT 25°

Potassium sulfate	6.96	Ammonium acetate	5.10
Potassium tartrate	7.00	Sodium succinate	7.64
Sodium malonate	7.98	Ammonium oxalate	6.35
Sodium citrate	7.60		

Measurement of Hydrogen Ion Activity.—The hydrogen ion activity was calculated from e. m. f. measurements made with a saturated quinhydrone electrode used in conjunction with a saturated calomel half cell at 25°. Readings were taken with a Leeds and Northrup portable type potentiometer.

The Effect of the Anions on *P*H of Solutions and Hydrosol

The work of Thomas and Whitehead[1] relative to the effect of sulfate ion on aluminum salt solutions was repeated and results similar to theirs obtained. However, these investigators did not take into consideration the effect of dilution and did not hold the concentration of aluminum constant. These two factors were held constant in all of our work, as was also done by Thomas and Tai[6] in their work on aluminum oxyiodide hydrosols. It need only be stated here that sulfate ion was the least effective ion studied in changing *P*H of aluminum solutions.

The volume used in our work was 100 cc., the aluminum content was 31 milliequivalents, and the temperature 25°.

TABLE III

THE EFFECT OF ANIONS ON THE *P*H VALUE OF ALUMINUM SALT SOLUTIONS

Normality of anion added	$AlCl_3$ *P*H	Δ*P*H	$Al(OH)Cl_2$ *P*H	Δ*P*H	$Al(OH)_2Cl$ *P*H	Δ*P*H
			Acetate			
0.0031	3.79	−0.24	3.94	−0.16	4.35	+0.05
.0250	4.25	+0.22	4.37	+0.27	4.81	+0.51
			Tartrate			
0.0300	3.27	−0.76	4.30	+0.20	5.38	+1.08
.2500	5.03	+1.00	5.23	+1.13	6.20	+1.90
			Citrate			
0.0078	2.98	−0.96	3.60	−0.47	5.04	+0.86
.2500	6.16	+2.22	6.53	+2.46	7.28	+3.10

Table III shows the effect of acetate, tartrate and citrate ions at different concentrations on the *P*H of

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[1] Thomas and Whitehead, *J. Phys. Chem.*, **35**, 27 (1931).

[2] Thomas and von Wicklen, THIS JOURNAL, **56**, 794 (1934).

[3] Heyrovsky, *J. Chem. Soc.*, **117**, 21 (1920); Jones, Carnegie Institute of Washington, Publ. No. 170; Miller, *U. S. Public Health Rpts.*, **40**, 361 (1925); Wilson and Kuan, *J. Am. Leather Chem. Assoc.*, **25**, 15 (1930); Miller, "Colloid Symposium Monograph," The Chemical Catalog Co., New York, 1925, Vol. III, p. 212; Charriou, *Compt. rend.*, **176**, 1895 (1932).

[4] See, Stiasny and Grimm, *Collegium*, **691**, 505 (1927), and *Z. physik. Chem.*, **73**, 724 (1910).

[5] T. H. Whitehead, "Ion Interchanges in Aluminum Oxychloride Hydrosols," Dissertation, Columbia University, New York, 1930.

[6] Thomas and Tai, THIS JOURNAL, **54**, 841 (1932).

aluminum salt solutions. Many determinations at other concentrations were made but they showed the same general trend and these only are reported as they show the general trend. Δ*P*H is the change in *P*H of the original aluminum salt produced by the addition of the anion.

The more extensive data on the effect of oxalate, malonate and tartrate ions upon the *P*H of aluminum salt solutions and aluminum hydrosol are plotted in Figs. 1, 2 and 3.

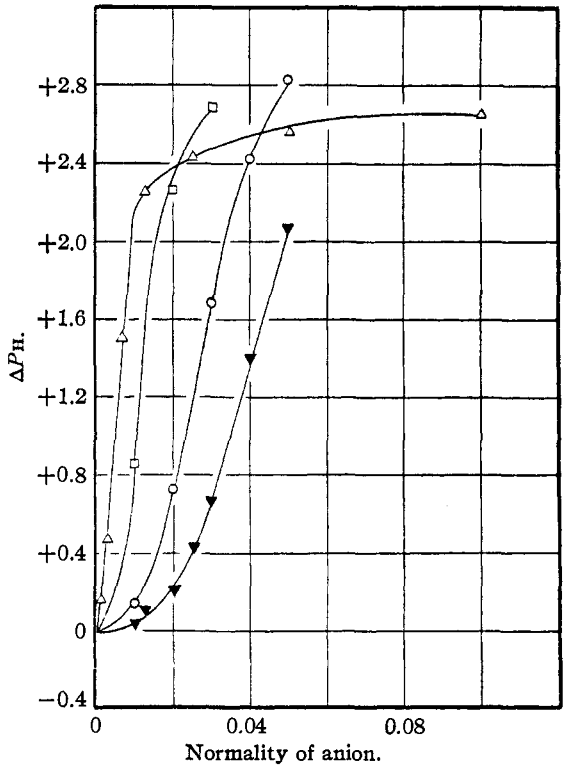

Fig. 1.—Effect of ammonium oxalate on *P*H of aluminum salt solutions and *aluminum* hydrosol: △, sol, □, $Al(OH)_2Cl$, ○, $Al(OH)Cl_2$, ▼, $AlCl_3$.

Discussion of Results Obtained

All of the results obtained show that any given anion affected the *P*H of the aluminum salt solutions and hydrosol in the order: hydrosol > $Al(OH)_2Cl$ > $Al(OH)Cl_2$ > $AlCl_3$, when the *P*H was increased.

They also show that for any aluminum salt solution or hydrosol the effectiveness of the anions in changing *P*H was: oxalate > citrate > malonate > tartrate > succinate > acetate > sulfate.

In some few cases the *P*H of the aluminum salt solution was at first decreased by the addition of anion and then as the concentration of anion became greater, the *P*H was increased and continued to increase.

The anion order obtained agrees with that of Stiasny,[7] who worked with basic chromium salts; with Whitehead[5] who worked with aluminum oxychloride hydrosols; with Todd,[8] who worked with aluminum oxybromide hydrosols, and with Thomas and von Wicklen,[2] who worked with chromium oxychloride hydrosols, except that they did not study malonate and succinate ions.

The failure of others[3] to explain their results by classical theories, buffer action, dilution or salt effect has been covered already.[1,2]

To explain our results it will be necessary to make certain assumptions. We assume that a salt of the type $AlCl_3 \cdot 6H_2O$ can be hydrolyzed in water solution according to the Werner–Pfeiffer idea, that the basic salt so produced can unite with other units to form "ol" and "μ-ol" complexes until aggregates of colloidal size can be produced. These are not original with the authors as Thomas Graham[9] expressed the belief that colloids are merely large aggregates of crystalloids. Many "ol" and "μ-ol" complexes were described for aluminum by Werner[10] and basic chromium salts with molecular weights of 750 have been described by Bjerrum.[11] The argument for this mechanism was ably presented by Thomas and von Wicklen,[2] assuming $CrCl_3 \cdot 6H_2O$ and $AlCl_3 \cdot 6H_2O$ to be analogous.

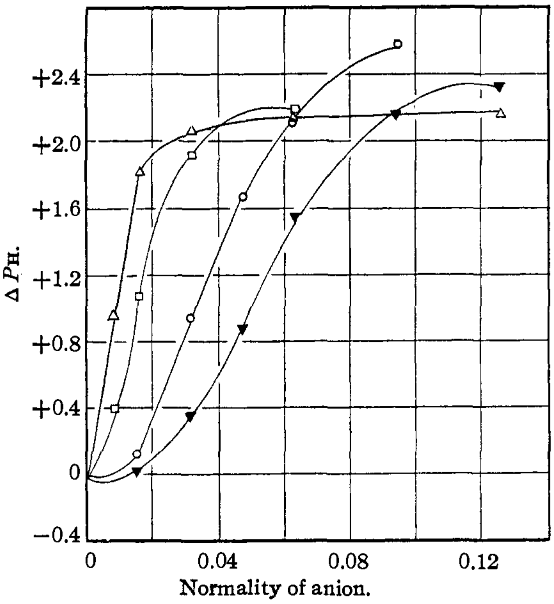

Fig. 2.—Effect of sodium malonate on *P*H of aluminum salt solutions and aluminum hydrosol: △, sol, □, $Al(OH)_2Cl$, ○, $Al(OH)Cl_2$, ▼, $AlCl_3$.

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[7] Stiasny and Szego, *Collegium*, **670**, 41 (1926).

[8] L. J. Todd, "A Study of Aluminum Oxybromide Hydrosols," Dissertation, Columbia University, New York, 1931.

[9] T. Graham, *Phil. Trans.*, **151**, 183 (1861).

[10] A. Werner, "New Ideas on Inorganic Chemistry" (English translation by E. P. Hedley) Longmans, Green and Co., 1911.

[11] See Stiasny and Grimm, *Collegium*, **691**, 505 (1927).

Thus the increased *P*H observed upon the addition of an anion is assumed to be the result of anion penetration into the "ol" complex with a forcing out of one or more hydroxo groups into the outer solution. But since aluminum salt solutions are not unique, the role of ions in increasing the hydrolysis of aluminum chloride solution cannot be ignored. Indeed when the concentration of an anion was so small as to make anion penetration negligible, a decreased *P*H was often observed and probably resulted from increased hydrolysis of the aluminum salt solution. This seems reasonable because $AlCl_3$ should be most affected because it is least basic, and $Al(OH)_2Cl$ least affected because it is most basic; this is exactly what occurred. That is, when *P*H was decreased the usual order was reversed. This also is to be expected because the number of hydroxy groups pushed out by an anion from the various aluminum solutions should vary as the number available for displacement and this number is greatest in the hydrosol and least in the $AlCl_3$.

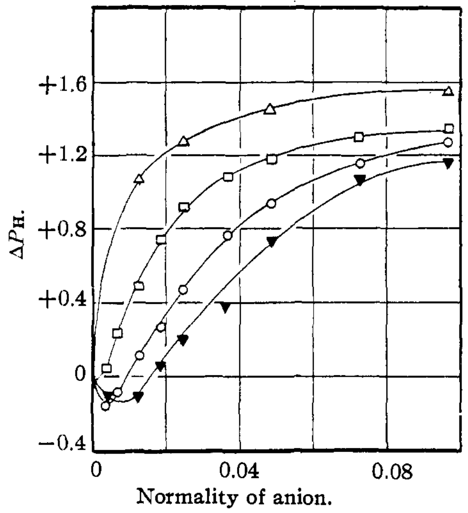

Fig. 3.—Effect of sodium succinate on *P*H of aluminum salt solutions and aluminum hydrosol: △, sol, □, $Al(OH)_2Cl$, ○, $Al(OH)Cl_2$, ▼, $AlCl_3$.

When anion penetration has ceased, it would be expected that the *P*H of the solution would be between that of the final solution and that of the added anion, *i. e.*, there would be little variation from the maximum reached and the curve would tend to flatten out. This is observed in the curves for the hydrosol and also in the aluminum salt solutions shown in Fig. 3, because succinate ion is a relatively weak penetrant and its penetration ceases sooner than malonate or oxalate.

The order oxalate, malonate, succinate is interesting because this is exactly the order of stability of cobalt complexes reported by W. Thomas[12] and our results agree if we assume that the most powerful penetrating ion forms the most stable complex as has been substantiated in the case of chromium salts by Stiasny and co-workers.[7,11] The great similarity of aluminum and chromium (3+) salt solutions makes this a reasonable assumption; however, the actual isolation and analysis of the complex aluminum salts is being done by the authors and will be reported when it is completed.

Summary

1. The various anions used decidedly decreased the hydrogen ion activity of crystalloid and colloid solutions at reasonably high concentrations of anions.
2. The effect of any anion studied upon the hydrogen-ion activity of solutions and sol was: sol > $Al(OH)_2Cl$ > $Al(OH)Cl_2$ > $AlCl_3$.
3. The order of effectiveness of the anions in increasing *P*H of any solution or sol was: oxalate > citrate > malonate > tartrate > succinate > acetate > sulfate.
4. There is no abrupt transition from simple aluminum chloride solution to the highly basic or colloidal ones.
5. These results can be explained by the Werner theory and its more recent extensions.

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[12] W. Thomas, "Complex Salts," Blackie and Sons, London, 1924, p. 107.