[A CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF KENTUCKY]

The Effect of Hydrogen-Ion Concentration on the Flocculation Values of Chromic and Aluminum Oxide Sols

BY M. HUME BEDFORD, W. H. KELLER AND J. L. GABBARD

Most of the previous investigations of the variation of flocculation values of hydrous oxide sols with hydrogen-ion concentration have been made in the presence of buffers and other contaminants,[1] or without a direct measure of the hydrogen-ion concentration.[2] But Hazel and Sorum[3] have devised a procedure for investigating the flocculation values of a series of hydrous oxide sols of gradually increasing and directly measured hydrogen-ion concentrations and free from any contaminating ions. This paper reports an application of their method to chromic and aluminum oxide sols.

The hydrogen-ion concentration was controlled by adding equal volumes of very dilute hydrochloric acid of slightly increasing concentrations to equal volumes of stock sols. Hydrogen-ion concentrations were measured by the use of the glass electrode and a vacuum tube voltmeter. Flocculation values were determined by adding equal volumes of the coagulating electrolyte of slightly increasing concentrations to samples of the sol until that concentration of electrolyte was found which, on standing for twenty-four hours, just produced complete coagulation.

Measurements.—Hydrogen-ion concentrations were determined potentiometrically. The glass electrode described by MacInnes and others[4] was used instead of the platinized hydrogen electrode. The glass electrode is greatly superior for this work because it is not poisoned by contaminants, does not tend to coagulate the sol or change its P_{H} value during measurements, and allows practically instantaneous readings.

Each glass electrode has a characteristic "asymmetry" potential which is large (as high as several volts) just after the electrode is made, but which gradually decreases to about 0.1 volt while the electrode is "aged" by immersion in dilute hydrochloric acid for several days, and is fairly constant thereafter. This constant was determined for the electrode before and after each set of readings by the use of standard buffer solutions, as described by Hazel and Sorum.[3]

Buffers of KCl–HCl, P_{H} 2.2, NaAc–HAc, P_{H} 4.63, and KH_2PO_4–Na_2HPO_4, P_{H} 5.9 were used. The P_{H} values of the buffers were checked with a standard hydrogen electrode. The constant of the electrode checked by the buffers just before and after each set of readings always agreed to within 0.02 of a P_{H} unit. The constant is calculated by the equation: $P_{\text{H}} = (E\text{ (cell)} + C)/0.059$ at 25°, where C is the desired constant and E is the measured e. m. f. of the cell.[5]

---

(1) Harry B. Weiser and E. E. Porter, *J. Phys. Chem.*, **31**, 1383 (1927).

(2) S. Ghosh and N. R. Dhar, *idid.*, **29**, 659 (1925); **30**, 830 (1926). N. R. Dhar and V. Gore, *J. Indian Chem. Soc.*, **6**, 31 (1929), from *Chem. Abst.*, **23**, 2628 (1929).

(3) Fred Hazel and C. H. Sorum, THIS JOURNAL, **53**, 49 (1931).

(4) D. A. MacInnes and Malcolm Dole, *ibid.*, **52**, 29 (1930); D. A. MacInnes and Donald Belcher, *ibid.*, **53**, 3315 (1931).

(5) Because methods described in the literature for making glass electrodes are both meager and

The hydrogen electrode was coupled with a normal calomel electrode through a salt bridge. The e. m. f. of the completed cell was measured by a vacuum-tube voltmeter of the type described by Partridge.[6] A Leeds and Northrop Student Potentiometer was used in place of the voltmeter in the Partridge circuit.

Precipitating values were determined by adding 3 cc. of the electrolyte to 2 cc. of sol, shaking thoroughly, and permitting the mixture to stand, stoppered, for twenty-four hours. Increasing concentrations of electrolyte were prepared by adding stock electrolyte of convenient concentration (previously determined) by 0.1-cc. increments to a 3-cc. vessel, and diluting to the mark (3 cc.) with distilled water. That concentration which just produced complete coagulation in twenty-four hours was taken as the flocculation value of the sol toward that electrolyte expressed in millimoles of electrolyte per liter of mixture.

This definition of the coagulating value is entirely arbitrary and was used merely as a matter of convenience. The values obtained are only relative, but are of less than 3.33% error with respect to each other. This limit of error is due to the fact that precipitants were added in 3.33% increments of concentration. That the values are valid relatively within this limit was demonstrated experimentally by the failure of 3.33% less electrolyte to produce complete coagulation, even when the sol so treated was left standing for several days.

With univalent and bivalent anions coagulation was usually quite definite. When a perfectly colorless layer of water one millimeter or more in depth was observable above the settling precipitate, coagulation was always found to be complete. This was shown by centrifuging for fifteen minutes at 1500 to 2500 r. p. m. and testing the supernatant liquid qualitatively for the metal. The salts of trivalent cations such as ferric, chromic, and aluminum ions produced a troublesome partial sedimentation very difficult to detect visually, the coagulum even being repeptized on centrifuging. It was necessary to repeat such precipitations until a qualitative test definitely indicated complete coagulation. The aluminum oxide sol particularly produced partial sedimentations which were very difficult to distinguish from complete coagulations because of the practically colorless nature of the sol. In such instances the samples were allowed to stand longer than twenty-four hours to let the coagulum settle further so that a sufficiently large quantity of the supernatant liquid could be drawn off for examination by the aluminon test.

Preparation of Sols.—The chromic oxide sol was prepared by hydrolysis of chromic chloride with boiling distilled water[7] and hot dialysis[8] through cellophane.[9] Dialysis was conducted at 85 to 90° for about twelve to fourteen hours per day for three weeks. At the conclusion of the dialysis, when treated with silver nitrate, distilled water which had stood overnight in contact with the sol through the cellophane failed to show any trace whatever of chloride ion. A sample of the sol dissolved in hot nitric acid showed a very faint cloudiness with silver nitrate due to the chloride ion adsorbed by the micelles. The sol contained 1.35 g. of chromium per liter and its P_H value at the conclusion of dialysis was found to be 6.4.

---

difficult, a new and ingenious process was devised which produced a stronger electrode and saved much time. By careful suction applied by the mouth to a rubber tube attached to the electrode tube, the glass membrane is gently drawn against and fused onto the hot end of the electrode tube held just above it, thus producing an electrode which because its inner surface is convex, is consequently stronger than those with plane surfaces obtained by the methods previously described. MacInnes and Belcher suggest that only one electrode be made from each bubble, but the writers found that by the above procedure a number of electrodes could be made from the pieces of each bubble. Fairly thick (not iridescent) membranes were also found to be quite efficient.

(6) H. M. Partridge, THIS JOURNAL, **51**, 1 (1929).

(7) Marks Neidle and Jacob Barab, *ibid.*, **39**, 71 (1917).

(8) Marks Neidle, *ibid.*, **38**, 1270 (1916).

(9) J. W. McBain and S. S. Kistler, *J. Phys. Chem.*, **35**, 130 (1931).

The aluminum oxide sol was prepared by precipitation and repeptization of aluminum hydroxide from a solution of aluminum chloride[10] and was dialyzed in a Neidle dialyzer using cellophane bags. The dialysis was conducted at 70 to 90° continuously for one week. Distilled water was allowed to flow through the cellophane bag at the rate of about 1 liter per hour. The dialyzed sol did not give a test for the aluminum ion by the aluminon test, and gave only a very slight test for the chloride ion with silver nitrate. The concentration of the sol was 1.652 g. of aluminum per liter and its *P*H value at the conclusion of dialysis was 5.85.

Data and Discussion of Results.—The writers repeated the work of Hazel and Sorum on ferric oxide sols, using two different stock sols each prepared according to the procedure of Hazel and Sorum. The flocculation values obtained were lower than those of Hazel and Sorum but the trends shown by the variations of flocculation values with hydrogen-ion concentration agreed completely with their results and substantiate fully their conclusions.

Tables I and II present the coagulation values of typical electrolytes toward chromic oxide and aluminum oxide sols, respectively.

TABLE I

FLOCCULATION VALUES IN MILLIMOLES PER LITER OF CHROMIC OXIDE SOLS CONTAINING 1.35 G. OF Cr PER LITER

Sols	1	2	3	4	5
*P*H	5.3	4.9	4.5	4.0	3.5
Electrolyte					
KBr	5.0	8.0	16.0	30.0	...
$^1/_3AlCl_3$	600.0	600.0	600.0	640.0	No ppt.
K_2SO_4	0.136	0.16	0.24	0.32	0.56
$CaSO_4$	.112	.124	.192	.24	.48
$K_3Fe(CN)_6$	.064	.076	.12	.17	.31
$K_4Fe(CN)_6$	.044	.060	.088	.12	.30

TABLE II

FLOCCULATION VALUES IN MILLIMOLES PER LITER OF ALUMINUM OXIDE SOLS CONTAINING 1.22 G. Al PER LITER

Sol	1	2	3	4	5
*P*H	5.67	5.22	4.74	4.40	3.96
Electrolyte					
KCl	26.0	30.0	34.0	46.0	100.0
K_2SO_4	0.34	0.40	0.44	0.50	0.60
$K_3Fe(CN)_6$	.13	.15	.16	.18	.19
$K_4Fe(CN)_6$	.096	.108	.13	.17	.18
K_2CrO_4	.30	...	.40	..	1.04
$^1/_2BaCl_2$	32.0	...	40.0	..	80.0
$^1/_3AlCl_3$	80.0	...	..	..	100.0

The electrolytes are salts of uni-, bi-, tri-, and quadrivalent anions, since ferric, chromic and aluminum oxide sols are positive, and the anion the component of the solution most active in coagulation.

[10] Harry B. Weiser, *J. Phys. Chem.*, **35**, 1368 (1931).

With two exceptions the stability of ferric oxide sol was found to vary directly with its hydrogen-ion concentration; in one case, the stability of ferric oxide sol toward sulfate ion decreased with increase of hydrogen-ion concentration; in the other case the flocculation values of the salts of trivalent metals, such as iron, chromium and aluminum, were constant within certain limits of *P*H values of sol samples. These results were obtained by Hazel and Sorum, and verified by the writers.

Chromic and aluminum oxide sols showed no exceptions whatever to the general rule that sol stability increases with increased hydrogen-ion concentration, within the limits investigated. However, the precipitating value of ferric chloride toward chromic oxide sol was constant from *P*H 5.3 to 4.5 but increased from *P*H 4.5 to 4.0, while at *P*H 3.5 ferric chloride failed entirely to coagulate the sol. This was probably due to the solution of the sol micelles in the quantity of acid from the hydrolysis of the salt added to the already considerable hydrogen-ion content of the sol.

The *P*H values of the sol samples after complete coagulation were also measured, but the trends shown by the results obtained were quite discordant and entirely unpredictable. These changes of *P*H values may have occurred at the time of mixing of electrolyte with the sol since the two systems were not isohydric, as was shown by comparison of the *P*H values of the electrolytes with those of the sols; or, the changes may have occurred during coagulation as a result of the processes accompanying coagulation; or, they may have resulted from both the mixing and the coagulation. Hence the *P*H values assigned to the sols may not represent the *P*H's at which coagulation occurred, but merely the original *P*H values of the sols. However, conclusions based on these data are perfectly valid regarding the stability toward electrolytes of these sols of the given *P*H values. Sufficient data were not collected during this investigation to determine the time of change of the *P*H values of the mixtures, and this problem is now being further investigated in this Laboratory.

Summary

1. The stability of chromic and aluminum oxide sols toward electrolytes has been shown to vary directly with their hydrogen-ion concentration.

2. The stability of ferric oxide sol varies directly with its hydrogen-ion concentration except toward sulfates, in which case the stability varies inversely with the hydrogen-ion concentration.

3. Ferric and aluminum chlorides have been shown to have constant precipitation values toward hydrous oxide sols, within certain limits of *P*H values, probably due to the maintenance of constant hydrogen-ion concentration by buffer action of the hydrolyzed salts.

LEXINGTON, KENTUCKY

RECEIVED APRIL 14, 1933
PUBLISHED OCTOBER 6, 1933