[Contribution from the Department of Chemistry, Columbia University, No. 614]

FERRIC OXYBROMIDE HYDROSOLS

By Arthur W. Thomas and Edna R. Hamburger

Received May 17, 1929 Published February 6, 1930

In a study of the behavior of ferric oxychloride hydrosols[1] previously reported[2] from this Laboratory, it was suggested that the nature of the anion was dominant in the behavior of hydrosols of this type. For example, while a ferric oxychloride hydrosol can be diluted with alcohol without precipitation of the dispersed phase, the addition of alcohol to a ferric oxysulfate hydrosol provokes instant precipitation. This is in accordance with the fact that chlorides in general are soluble in alcohol while sulfates are not. The above mentioned difference between ferric oxychloride and ferric oxysulfate hydrosols together with quantitatively measured behavior of ferric oxychloride sols on dialysis led to the contention that the stability of "ferric oxide" hydrosols resides in the solution forces of the ferric salts or of the basic ferric salts which are part of the colloidal aggregate.[2]

A chemical mechanism accounting for the precipitation of ferric oxychloride hydrosols by silicic acid–sodium silicate and arsenious sulfide–hydrogen sulfide hydrosols was also offered[3] showing that the chemical nature of all ions of a hydrosol must be reckoned with rather than merely considering the charge of the colloidal micelle. This idea is not new; Linder and Picton[4] in 1892 suggested that "the aggregates of ferric hydrate are held in solution almost entirely by their loose union with surrounding molecules of ferric chloride, themselves in a state of more perfect solution." In 1905 they concluded that the colloid was an hydroxychloride and not a hydrate associated with ferric chloride or free hydrochloric acid.

In this connection it is interesting to note that Freundlich and Wosnessensky[5] prepared a ferric oxide hydrosol by oxidizing a solution of iron carbonyl with hydrogen peroxide. Boiling the sol for a few minutes precipitated it; bubbling carbon dioxide through the coagulum repeptized it—this sol possesses the properties of a bicarbonate.

The present investigation was undertaken with the aim of extending

---

[1] While sols of this type are generally described as hydrous ferric oxide peptized by certain cations, it is necessary in this paper as a result of certain differences in properties caused by the anion of the peptizing electrolyte, to include the name of the anion. The name hydrous ferric oxide sol may be applied accurately only in one case described in the literature, *i. e.*, the dispersion prepared and described by C. H. Sorum, This Journal, **50**, 1263 (1928).

[2] Thomas and Frieden, *ibid.*, **45**, 2522 (1923).

[3] Thomas and Johnson, *ibid.*, **45**, 2532 (1923).

[4] Linder and Picton, *J. Chem. Soc.*, **61**, 152, 165 (1892); **87**, 1718 (1905).

[5] Freundlich and Wosnessensky, *Kolloid-Z.*, **33**, 222 (1923).

the knowledge of the nature of "iron oxide" sols particularly from the angle of the "peptizing agent" which is responsible for and governs the stability and reaction of sols of the hydrous ferric oxide type. Ferric oxybromide sols were selected for this purpose.

Ferric oxybromide hydrosols have been known since 1859. In that year Ordway[6] reported that "bromohydric acid takes up at least five equivalents of ferric oxyd" and Béchamp[7] that ferric bromide dissolves gelatinous ferric hydroxide as readily as ferric chloride. The work of these two investigators seems to constitute the only account of ferric oxybromide hydrosols in the literature.

Preparation

Since ferric bromide is not readily available, Béchamp's method could not be used. At first an attempt was made to prepare the sols by peptizing the freshly precipitated ferric oxide obtained from a Graham ferric oxychloride sol (by addition of ammonium hydroxide) with hydrobromic acid, reprecipitating with ammonium hydroxide and repeptizing with hydrobromic acid until chloride ion was absent. This method proved unsatisfactory due to the difficulty of removing all traces of chloride and the following procedure, the oxidation of ferrous bromide by hydrogen peroxide, was adopted. This is the same as Neidle's[8] method of preparing ferric oxychloride sols.

The details of the method are as follows: to each 100-g. portion of pulverized iron[9] is added 500 cc. of 40% hydrobromic acid and one liter of distilled water. The mixture is heated gently and stirred constantly. As the rapid evolution of gas slows down somewhat the temperature may be raised. The reaction is assumed to be complete when the evolution of hydrogen ceases and oxidation to the ferric condition is just starting (as evidenced by traces of red, precipitated ferric oxide). The greenish-blue ferrous bromide solution is then filtered from the residual iron, carbon, etc., and oxidized by slowly adding hydrogen peroxide,[10] stirring constantly until ferrous ion test is negative. When approaching the end-point, the odor of free bromine is also observed. This free bromine is removed in the first twenty-four hours of dialysis.

Immediately after preparation, the sol is dialyzed against running water for twelve to twenty-four hours and then dialyzed against distilled water until the desired "purity" is obtained.

All sols dialyzing against distilled water, unless otherwise mentioned, were stirred by means of a current of compressed air washed with dilute sulfuric acid, dilute sodium hydroxide, passed through a column of glass beads and of absorbent cotton.

---

[6] Ordway, *Am. J. Sci.*, [2] **26**, 197 (1859).

[7] Béchamp, *Ann. chim. phys.*, [3] **57**, 296 (1859).

[8] Neidle, This Journal, **39**, 2334 (1917).

[9] Pulverized iron (of 99.7 to 99.9% purity) kindly furnished by the Hawthorne Works of the Western Electric Company was used. According to analysis supplied by the donor, the following impurities were present: carbon, 0.022–0.058%; sulfur, 0.003–0.013%; silicon, 0.034–0.117%; manganese, 0.023–0.048%; phosphorus, 0.004–0.028%.

[10] The proprietary "Dioxygen" was used.

Tests with Laar's[11] reagent (sulfuric acid solution of diphenylamine) for the presence of bromate, peroxide, etc., gave negative results with sols prepared in this fashion.

Ferric oxychloride hydrosols were prepared in the same manner, using 100 g. of pulverized iron, 200 cc. of concd. c. p. hydrochloric acid and 1200 cc. of distilled water.

Analytical Procedure

The analytical results herein reported are expressed in terms of milli-equivalents per liter. In all cases analyses were made for total iron and total halide content.

Iron.—A portion of the sol evaporated to fuming with sulfuric acid to remove all bromine was then diluted, reduced in a Jones reductor in the customary manner and titrated with standardized potassium permanganate solution.

Halide.—To a portion of the sol 10 cc. of 16 M nitric acid, 10 cc. of 0.1 M silver nitrate and water were added to a volume of 125 cc. This mixture was heated overnight at about 60° in a dark place.[12] Check analyses made on potassium bromide solutions proved that no bromine was lost by this method.

Comparative Behavior of Ferric Oxybromide and Ferric Oxychloride Hydrosols.—A series of sols of varying Fe/halide ratios was prepared and the following properties measured: sodium sulfate liminal value, viscosity and electrical conductivity. While attention was concentrated upon the ferric oxybromide sols, a sufficient number of ferric oxychloride hydrosols were studied, however, to enable comparisons to be drawn between the two. All sols were "pressure" dialyzed in nitrocellulose bags against distilled water at room temperature until the desired ratio of iron to halide was obtained. They were then diluted to a concentration of about 400 milli-equivalents of iron per liter.

Since it was found that ferric oxybromide sols hydrolyze readily, they were used as soon as feasible after being prepared.

By liminal value is meant the average in millimoles of the amount of a salt which just fails to precipitate and the amount which just does precipitate the sol under given conditions. The technique adopted was as follows: into one series of test-tubes were pipetted 5-cc. portions of the sol, and in another series of tubes were placed 5-cc. volumes of salt solutions of varying concentration. The electrolyte solution was added to the sol by pouring slowly down the side of the tube and the contents were mixed by inverting twice. The tubes were then centrifuged for two minutes at 1300 revolutions per minute (radius, 28 cm.). The end-point was judged to be the tube in which the supernatant solution above the precipitate was clear and colorless, the supernatant solution of the tube just preceding being a pale yellow, and that of the tube following also being clear and colorless. The values in the tables are the averages of the readings of two series of measurements.

---

[11] Laar, *Ber.*, **15**, 2086 (1882).

[12] It is interesting to note that freshly prepared sols are thus decomposed much more readily than aged ones. The former are decomposed in the cold, whereas the latter require the elevated temperature for decomposition in the time mentioned.

Viscosity measurements were made at 25 ± 0.1° in an Ostwald viscometer. Readings are recorded as time of outflow, since the only significance which they have is a comparative one. The outflow time for water was 80.0 seconds.

The conductivity measurements were made at 25 ± 0.01° using a Freas cell with polished platinum electrodes, a circulary slide wire bridge and variable air condensers. The source of the alternating current was a Leeds and Northrup Vreeland oscillator. When not in use the cells were kept short-circuited as advised by Morgan and Lammert.[13] Parker and Parker's[14] revised value for the specific conductivity of 0.01 N potassium chloride was employed in determining the cell constant. Certain difficulties were encountered, rendering the experimental error about ±2.5%.

The results obtained for ferric oxybromide hydrosols are recorded in

TABLE I

FERRIC OXYBROMIDE HYDROSOLS. CHANGE IN PROPERTIES AS RATIO FE/BR INCREASES

Fe/liter, 415 milli-equiv. Maximum time elapsing between end of dialysis and final measurement, two weeks.

Sol[a]	Fe/Br, equiv.	Na_2SO_4, liminal value, millimoles	Viscosity, sec. outflow	Conductivity, mhos × 10^6
44	20.4	7.47	86.0	656
44A	22.2	7.15	87.2	565
44B	25.6	6.12	87.9	419
42A	25.7	5.96	89.4	...
44D	29.8	5.00	91.5	293
42	33.5	4.24	92.3	...
44C	38.5	3.65	..	166
43	41.8	3.62	93.9	...

[a] Sols 44, 44A, 44B, 44C and 44D were all made from the same mother sol by further dialysis. Sols 42 and 42A came from a different mother sol and Sol 43 from a third mother sol.

TABLE II

FERRIC OXYCHLORIDE HYDROSOLS. CHANGE IN PROPERTIES AS THE RATIO FE/CL INCREASES

Fe/liter, 415 milli-equiv. Maximum time elapsing between end of dialysis and final measurement, two weeks.

Sol[a]	Fe/Cl, equiv.	Na_2SO_4, liminal value, millimoles	Viscosity, sec. outflow	Conductivity, mhos × 10^6
11	20.0	5.05	90.4	279
11F	23.1	3.94	92.3	218
11A	24.0	3.94	92.5	195
10	25.7	3.49	91.6	...
11E	30.3	2.67	92.0	153

[a] Sols 11, 11A, 11E and 11F were all prepared from the same stock sol, and Sol 10 from a second stock sol.

---

[13] Morgan and Lammert, THIS JOURNAL, **45**, 1672 (1923); **46**, 1117 (1924).

[14] Parker and Parker, *ibid.*, **46**, 312 (1924).

Table I and plotted in Fig. 1. Similar results for ferric oxychloride hydrosols are given in Table II and in Fig. 1.

The measurements charted in Fig. 1 were not carried beyond the ratio Fe/Cl = 30 due to irregularities caused by incipience of precipitation in the ferric oxychloride sols. Incipience of precipitation is not observed in ferric oxybromide hydrosols until the Fe/Br ratio is much greater.

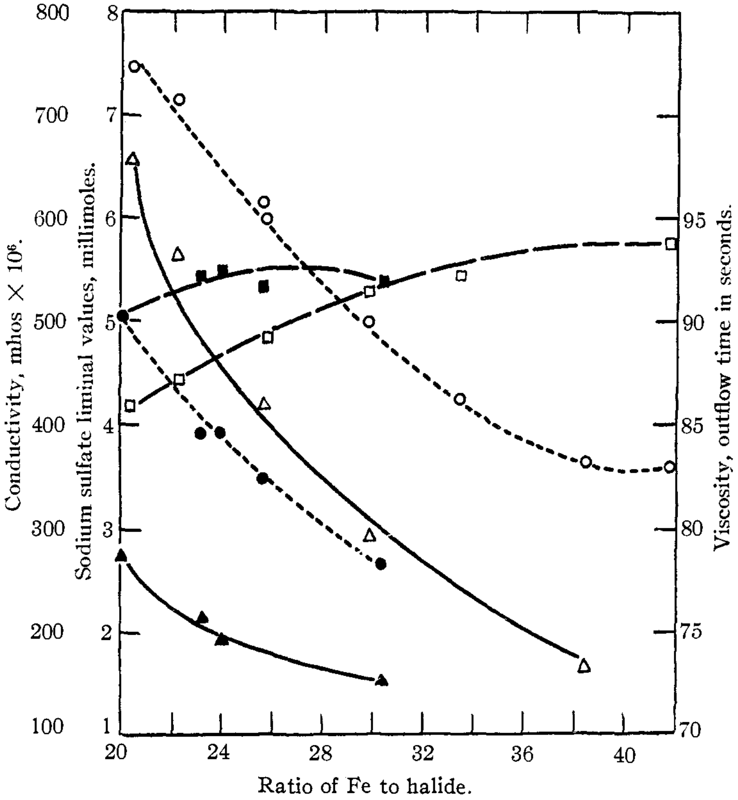

Fig. 1.—Variation of certain properties with variation of Fe : halide ratio. ●, Liminal values, ferric oxychloride sols; ○, liminal values, ferric oxybromide sols; ■, viscosities, ferric oxychloride sols; □, viscosities, ferric oxybromide sols; ▲, conductivities, ferric oxychloride sols; △, conductivities, ferric oxybromide sols.

It is seen that as the Fe/halide ratio increases, the conductivity and sodium sulfate liminal value decrease, while the viscosity increases in each case. In every case, however, at a given Fe/halide ratio the conductivity of a ferric oxychloride hydrosol is less than that of a ferric oxybromide sol, and the dispersed phase of a "chloride" sol is more easily salted out by sodium sulfate than the dispersed phase of a "bromide" sol.

Pairs of ferric oxybromide and oxychloride hydrosols were dialyzed simultaneously as nearly as possible to the same Fe/halide ratio and the concentrations then adjusted so that they were identical in each pair. Liminal values were then determined for sodium chloride, sodium bromide and sodium hydroxide, using the technique previously described. In order to obtain a sharply defined precipitate it was necessary to centrifuge the coagula caused by sodium chloride and sodium bromide for three minutes. For purposes of comparison, the liminal values for sodium sulfate are repeated from the previous tables. The results obtained are reported in Tables IIIA and IIIB.

TABLE III

LIMINAL VALUES FOR ELECTROLYTES ON FERRIC OXYCHLORIDE AND FERRIC OXYBROMIDE HYDROSOLS OF CORRESPONDING FE/HALIDE RATIO

A. SOLS PREPARED BY ROOM TEMPERATURE DIALYSIS

Sol	Fe/halide equiv.	Millimoles/liter				
		NaCl	NaBr	Na_2SO_4	NaOH	$K_4Fe(CN)_6$
Cl-10	25.7	162	395	3.49	6.76	. .
Br-42A	25.5	320	644	5.96	11.7	. .

Fe/liter = 415 milli-equiv.

B. SOLS PREPARED BY HOT DIALYSIS

Sol	Fe/halide equiv.	Millimoles/liter				
		NaCl	NaBr	Na_2SO_4	NaOH	$K_4Fe(CN)$
Cl-4P2	23.7	202	324	4.45	. . .	2.13
Br-37	24.4	381	787	6.37	. . .	3.25

Fe/liter = 440 milli-equiv.

The data in Table III show in general that ferric oxybromide sols are less easily salted out than corresponding[15] ferric oxychloride sols.

Aging Experiment.—Ferric oxybromide hydrosols when freshly prepared are clear brownish-red when viewed by either reflected or transmitted light. It was noticed that after such sols stand at room temperature for about six months they assume a turbid appearance to reflected light while still clear brownish-red to transmitted light. From past experience with ferric oxychloride sols in this Laboratory, it is known that the latter undergo such a change only after several years' standing.

Repeatedly in the preparation of these sols it has been noticed that ferric oxychloride hydrosols require at least twice the time to reach a given Fe/halide ratio by dialysis that ferric oxybromide sols do, thus indicating a greater rate of hydrolysis of the latter. Evidence for greater degree of hydrolysis is suggested by the fact that while ferric oxychloride sols of the concentration and Fe/Cl ratio studied here show a *P*H value of 4.9,[2] the *P*H value of similar freshly prepared ferric oxybromide hydrosols is indicated to be about 3, by means of the quinhydrone electrode, taking initial potentials.

---

[15] The word *corresponding* is used here and subsequently to mean hydrosols of the same total iron content and like ratio of total iron to total halide.

Several hydrosols were submitted to accelerated aging by enclosing in securely stoppered pyrex glass containers which were placed in an oven at 90 ± 2°. The results for two hydrosols are recorded in Tables IV and V and in Fig. 2.

The increase in conductivity and the decrease in viscosity upon heating indicate that the micelles undergo hydrolysis and dehydration. Comparing the curves for the two sols, it is seen that ferric oxybromide hydrosol micelles hydrolyze much more rapidly than ferric oxychloride micelles.

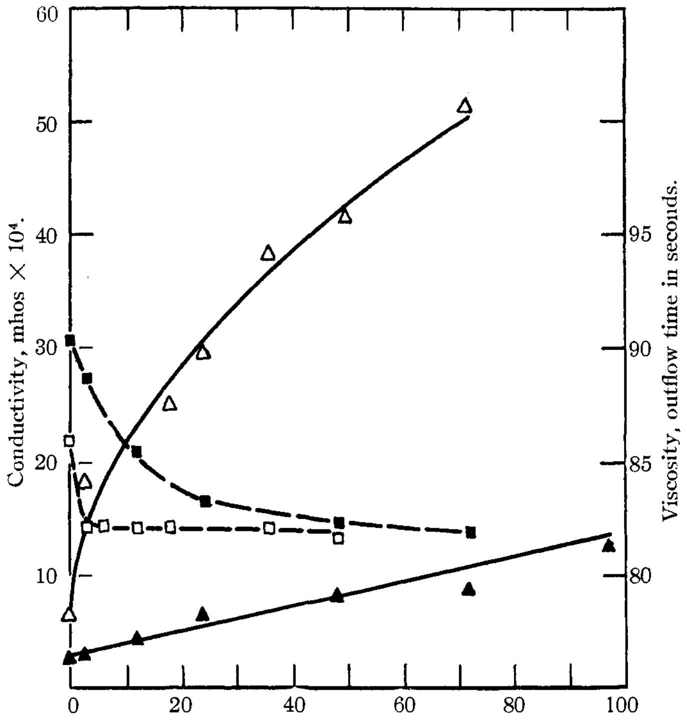

Fig. 2.—Change in certain properties as a function of time at 90°. ■, Viscosity, ferric oxychloride sol; □, viscosity, ferric oxybromide sol; ▲, conductivity, ferric oxychloride sol; △, conductivity, ferric oxybromide sol.

It will be recalled that the data in Tables I and II indicate that ferric oxybromide sols are hydrolyzed to a greater extent than corresponding ferric oxychloride sols.

Since the viscosity of a given ferric oxyhalide sol varies with degree of hydrolysis, it is evident that the ratio of iron to halide is insufficient for exact definition of a hydrosol of this type.

Greater hydrolysis of the dispersed phase results in micelles richer in

TABLE IV

AGING OF FERRIC OXYBROMIDE HYDROSOL NO. 44[a]

Heated, hours	Appearance[c]	Visc., sec. outflow	Cond., mhos × 10^5
0	A	86.0	66
3	B	82.1	183
12	B	82.1	...
18	D	82.1	250
24	E	81.7	295
36	F	82.1	383
48	G	..	419
72	G	..	514
90	H	..	...

[a] The concentration was 415 milliequivalents of Fe per liter; ratio Fe/Br = 20.4.

TABLE V

AGING OF FERRIC OXYCHLORIDE HYDROSOL NO. 11[b]

Heated, hours	Appearance[c]	Visc., sec. outflow	Cond. mhos × 10^5
0	A	90.4	28
3	B	87.6	29
12	B	85.0	45
24	B	83.3	63
48	C	82.4	83
72	F	..	89
97	G	..	125
120	G	..	131
1 month	H	..	...

[b] Same concentration as Sol 44; ratio Fe/Cl = 20.0.

[c] The key letters under "appearance" have the following significance: A, characteristic color; B, redness of characteristic color intensified; C, B plus slight yellow precipitate; D, brownish turbidity to reflected light just starting; E, chocolate brown to reflected light, clear red brown to transmitted light; F, chocolate or orange brown somewhat turbid to transmitted light, yellow sediment; G, orange, absolutely opaque, usually a layer of clear red sol above and a layer of yellow sediment; H, complete precipitation, orange, finely divided solid covered with clear supernatant liquor which gives a positive test for halide ion.

ferric oxide and poorer in halide, and consequently less stable, yet more sodium sulfate is required for the salting out of ferric oxybromide sols than for corresponding ferric oxychloride sols despite the greater hydrolysis of the former, thus showing the significance of the anion or anionogen upon the properties of sols of the ferric oxide type.

Summary

1. As the ratio of iron to halide in ferric oxybromide and ferric oxychloride hydrosols diminishes, the viscosity increases while the liminal value and electrical conductivity decrease.
2. Ferric oxybromide sols have higher electrical conductivities than corresponding ferric oxychloride sols.
3. The micelles of ferric oxybromide sols appear to hydrolyze more readily and to a greater extent than those of corresponding ferric oxychloride sols.
4. The dispersed phase of ferric oxychloride sols is more easily salted out than that of the corresponding ferric oxybromide sols.

NEW YORK, N. Y.