

CHARGE AND STABILITY OF COLLOIDS. PART IX.
STUDIES ON THE RELEASE OF COUNTER IONS
FROM $\text{Fe}(\text{OH})_3$ SOL ON THE ADDITION OF PAIRS
OF ELECTROLYTES

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The effect of the addition of pairs of electrolytes on release of counter ions from $\text{Fe}(\text{OH})_3$ sol has been studied. It has been found that in almost all cases the amount of released chlorine is greater than the calculated value. This means that the mixture induces more instability a necessary consequence of which is that there should be no ionic antagonism.

Recently various attempts have been made by several authors (Weiser, *J. Phys. Chem.*, 1931, 35, 1, 1368; Rabinowitsch, *Z. physikal. Chem.*, 1925, 116, 97; and Pauli and others) to follow the changes in the stability of a colloid on the stepwise addition of an electrolyte by determining the amount of counter ions released potentiometrically. In this paper attempts have been made to study the effects of pairs of electrolytes by the above method.

In earlier papers of this series (*J. Indian Chem. Soc.*, 1943, 20, 115, 219, 223) the release of the counter ions has been studied in some details, when electrolytes having ions of varying valencies are added in single to the hydrous sols of different purity. In this paper the release of counter ions from ferric hydroxide sol has been studied with a view to finding out if any insight into the mechanism of coagulation by electrolyte pairs can be obtained. Electrolyte pairs like $\text{KIO}_3 + \text{K}_2\text{SO}_4$; $\text{KIO}_3 + \text{K-citrate}$; $\text{K}_2\text{SO}_4 + \text{K-citrate}$ have been used. Along with this the release of chlorine ions, when KIO_3 , K_2SO_4 and K-citrate are added in singles, is also recorded.

EXPERIMENTAL

Ferric hydroxide sol was prepared by the method given in earlier section of this series (*J. Indian Chem. Soc.*, 1943, 20, 25, 115). The potentiometric titrations were performed exactly as described before. The volume of the sol taken in each case was 5 c.c., and the total volume of sol and electrolyte mixture was made up to 10 c.c. by adding the requisite volume of distilled water. The maximum amount of the electrolyte added to the fixed volume of the sol was just sufficient to coagulate the sol in an hour. The results obtained are given in the following tables. In these tables the electrolytes have been added up to the coagulation concentration *i.e.*, the last figure denotes the coagulation concentration.

TABLE I

Chlorine displaced from $\text{Fe}(\text{OH})_3$ sol when $N/10\text{-KIO}_3$ is added to it.

$N/10\text{-KIO}_3$ added,	π	$\alpha\text{Cl} \times 10^3$	Total $[\text{Cl}] \times 10^3$	$[\text{Cl}]$ displ. $\times 10^3$	$[\text{Cl}]$ eqvt. to $[\text{IO}_3] \times 10^3$
0.00 c.c.	0.1012 volts	1.54	1.58	0.00	0.00
0.50	0.0981	1.74	1.79	0.21	5.00
1.00	0.0843	2.02	2.10	0.82	10.00
1.50	0.0916	2.24	2.38	0.75	15.00
2.00	0.0890	2.48	2.60	1.02	20.00
2.50	0.0855	2.84	2.99	1.41	25.00
3.00	0.0831	3.12	3.30	1.72	30.00

TABLE II

Chlorine displaced from $\text{Fe}(\text{OH})_3$ sol when $N/50\text{-K}_2\text{SO}_4$ is added to it.

$N/50\text{-K}_2\text{SO}_4$ added,	π	$\alpha\text{Cl} \times 10^3$	Total $[\text{Cl}] \times 10^3$	$[\text{Cl}]$ displ. $\times 10^3$	$[\text{Cl}]$ eqvt. to $[\text{SO}_4] \times 10^3$
0.00 c.c.	0.1012 volts	1.54	1.58	0.00	0.00
0.50	0.0922	2.19	2.28	0.70	1.00
1.00	0.0863	2.76	2.89	1.31	2.00
1.50	0.0838	3.04	3.20	1.61	3.00
2.00	0.0805	3.45	3.65	2.07	4.00
2.50	0.0786	4.52	4.81	3.23	5.00
3.00	0.0697	5.26	5.63	4.05	6.00

TABLE III

Chlorine displaced from $\text{Fe}(\text{OH})_3$ sol when $N/200\text{-K-citrate}$ is added.

$N/200\text{-K-citrate}$ added,	π	$\alpha\text{Cl} \times 10^3$	Total $[\text{Cl}] \times 10^3$	$[\text{Cl}]$ displ. $\times 10^3$	$[\text{Cl}]$ eqvt. to $[\text{Citrate}] \times 10^3$
0.00 c.c.	0.1012 volts	1.54	1.58	0.00	0.00
1.00	0.0965	1.72	1.76	0.18	0.50
2.00	0.0965	1.85	1.91	0.33	1.00
3.00	0.0935	2.08	2.15	0.57	1.50
4.00	0.0885	2.53	2.63	1.05	2.00
4.50	0.0825	3.20	3.33	1.75	2.25
5.00	0.0755	4.20	4.44	2.86	2.50

TABLE IV

Chlorine displaced from $\text{Fe}(\text{OH})_3$ sol on adding $N/50\text{-K}_2\text{SO}_4 + N/10\text{-KIO}_3$.

0.5 c.c. $\text{K}_2\text{SO}_4 + \text{KIO}_3$	π	$\alpha\text{Cl} \times 10^3$	Total $[\text{Cl}] \times 10^4$	$[\text{Cl}] \text{ displ.} \times 10^3$	$[\text{Cl}] \text{ eqvt. to } [\text{SO}_4] \text{ \& } [\text{IO}_3] \times 10^3$
0.00 c.c.	0.1012 volts	1.54	1.58	0.00	0.00
0.25	0.0911	2.03	2.10	0.52	3.50
0.50	0.0894	2.44	2.53	0.95	6.00
1.00	0.0845	2.96	3.08	1.50	11.00
1.50	0.0809	3.40	3.56	1.98	16.00
1.75	0.0785	3.73	3.92	2.31	18.50
2.00	0.0768	3.99	4.21	2.63	21.00

TABLE V

Chlorine displaced from $\text{Fe}(\text{OH})_3$ sol on adding $N/200\text{-K-citr.} + N/10\text{-KIO}_3$.

1 c.c. $\text{K-citr} + \text{KIO}_3$	π	$\alpha\text{Cl} \times 10^3$	Total $[\text{Cl}] \times 10^3$	$[\text{Cl}] \text{ displ.} \times 10^3$	$[\text{Cl}] \text{ eqvt. to } [\text{Citr.}] \text{ \& } [\text{IO}_3] \times 10^3$
0.00 c.c.	0.1012 volts,	1.54	1.58	0.00	0.00
0.25	0.0957	1.91	1.97	0.39	3.00
0.50	0.0934	2.09	2.16	0.58	5.50
1.00	0.0907	2.32	2.40	0.82	10.50
1.50	0.0862	2.77	2.88	1.30	15.50
2.00	0.0814	2.97	3.08	1.50	20.50
2.50	0.0772	3.93	4.12	2.54	25.50

TABLE VI

Chlorine displaced from $\text{Fe}(\text{OH})_3$ sol on adding $N/10\text{-KIO}_3 + N/50\text{-K}_2\text{SO}_4$.

1 c.c. $\text{KIO}_3 + \text{K}_2\text{SO}_4$	π	$\alpha\text{Cl} \times 10^3$	Total $[\text{Cl}] \times 10^3$	$[\text{Cl}] \text{ displ.} \times 10^3$	$[\text{Cl}] \text{ eqvt. to } [\text{IO}_3] \text{ \& } [\text{SO}_4] \times 10^3$
0.00 c.c.	0.1012 volts	1.54	1.58	0.00	0.00
0.10	0.0928	2.14	2.23	0.66	10.20
0.20	0.0856	2.83	2.97	1.39	10.40
0.40	0.0807	3.43	3.63	2.05	10.80
0.60	0.0766	4.18	4.41	2.83	11.20
0.80	0.0704	5.12	5.48	3.90	11.60
1.00	0.0628	6.84	7.44	5.86	12.00

TABLE VII

Chlorine displaced from $\text{Fe}(\text{OH})_3$ sol on adding $N/200\text{-K-cit.} + N/50\text{-K}_2\text{SO}_4$.

0.5 c.c. K-citr + K_2SO_4	π	$\alpha\text{Cl} \times 10^3$	Total $[\text{Cl}] \times 10^3$	$[\text{Cl}]$ displ. $\times 10^3$	$[\text{Cl}]$ eqvt. to $[\text{Citr}]$ & $[\text{SO}_4] \times 10^3$
0.00 c.c.	0.1012 volts	1.54	1.58	0.00	0.00
0.10	0.0986	1.71	1.76	0.18	0.45
0.30	0.0968	1.83	1.89	0.31	0.85
0.60	0.0921	2.20	2.29	0.71	1.45
0.90	0.0868	2.71	2.81	1.23	2.05
1.20	0.0820	3.26	3.45	1.87	2.65
1.50	0.0769	4.13	4.40	2.82	3.25

TABLE VIII

Chlorine displaced from $\text{Fe}(\text{OH})_3$ sol on adding $N/10\text{-KIO}_3 + N/200\text{-K-cit.}$

1 c.c. KIO_3 + K-cit.	π	$\alpha\text{Cl} \times 10^3$	Total $[\text{Cl}] \times 10^3$	$[\text{Cl}]$ displ. $\times 10^3$	$[\text{Cl}]$ eqvt. to $[\text{SO}_4]$ & $[\text{Cit}] \times 10^3$
0.00 c.c.	0.1012 volts	1.54	1.58	0.00	0.00
0.50	0.0914	2.26	2.36	0.78	10.25
1.00	0.0842	2.99	3.16	1.57	10.50
2.00	0.0827	3.17	3.35	1.77	11.00
2.50	0.0806	3.44	3.65	2.07	11.25
3.00	0.0775	3.88	4.13	2.65	11.50
4.00	0.0753	4.23	4.51	2.93	12.00

TABLE IX

Chlorine displaced from $\text{Fe}(\text{OH})_3$ sol on adding $N/50\text{-K}_2\text{SO}_4 + N/200\text{-K-citrate.}$

0.5 c.c. K_2SO_4 + K-citr.	π	$\alpha\text{Cl} \times 10^3$	Total $[\text{Cl}] \times 10^3$	$[\text{Cl}]$ displ. $\times 10^3$	$[\text{Cl}]$ eqvt. to $[\text{SO}_4]$ & $[\text{Cit}] \times 10^3$
0.00 c.c.	0.1012 volts	1.54	1.58	0.00	0.00
0.50	0.0932	2.11	2.18	0.60	1.25
1.00	0.0886	2.52	2.62	1.04	1.50
2.00	0.0867	2.72	2.83	1.25	2.00
2.50	0.0852	2.88	3.02	1.44	2.25
3.00	0.0841	3.00	3.13	1.55	2.50
4.00	0.0810	3.39	3.55	1.97	3.00

DISCUSSIONS.

From the above results the following tables have been calculated.

Concentration of $\text{Fe}(\text{OH})_3$ sol, as $\text{Fe}_2\text{O}_3 = 9.018$ g/litre.

Chlorine content of the sol = 0.012 g. ion/litre.

Purity of the sol i.e., $\text{Fe}_2\text{O}_3/\text{Cl} = 751.0$.

TABLE X

Displacement of chlorine ions from $\text{Fe}(\text{OH})_3$ sol by ions of different valency.

Electrolyte added.	Displacement of [Cl] to electro-lyte added	[Cl] equiv. to electro-lyte added	Electrolyte added.	Displacement of [Cl] to electro-lyte added	[Cl] equiv. to electro-lyte added	Electrolyte added.	Displacement of [Cl] to electro-lyte added	[Cl] equiv. to electro-lyte added
	$(\text{OH})_3$ sol $\times 10^3$.	$\times 10^3$.		$(\text{OH})_3$ sol $\times 10^3$.	$\times 10^3$.		$(\text{OH})_3$ sol $\times 10^3$.	$\times 10^3$.
	N/10-KIO ₃			N/50-K ₂ SO ₄			N/200-K-citrate	
0.50 c.c.	0.21	5.00	0.50 c.c.	0.70	1.00	0.50 c.c.	0.18	0.50
1.00	0.52	10.00	1.00	1.31	2.00	1.00	0.33	1.00
1.50	0.76	15.00	1.50	1.61	3.00	1.50	0.57	1.50
2.00	1.02	20.00	2.00	2.07	4.00	2.00	1.05	2.00
2.50	1.41	25.00	2.25	3.23	4.50	2.25	1.75	2.25
3.00	1.72	30.00	2.50	4.05	5.00	2.50	2.86	2.50

From the above table it will be seen that the amount of chlorine displaced in the case of ferric hydroxide sol increases with K_2SO_4 as compared to KIO_3 , and then again decreases with K-citrate. This can be explained on the basis of the purity of the sol. We have observed previously that with these sols there is always a certain purity after which chlorine ions released is less than the equivalent of the added electrolyte, whereas with less pure sols the released chlorine is greater than the added electrolyte. The ferric hydroxide sol is purer than this limit.

A result similar to the one observed here was obtained by Weiser (*J. Phys. Chem.*, 1931, 35, 9) with ferric hydroxide sol, using KNO_3 , K_2SO_4 , K-citrate and $\text{K}_3\text{Fe}(\text{CN})_6$. In his case also, with uni-univalent electrolyte the displaced chlorine was the lowest, then it suddenly increased when K_2SO_4 was used and decreased again in the case of K-citrate and $\text{K}_3\text{Fe}(\text{CN})_6$. In Weiser's case also, a similar effect is noticed as $\text{Fe}(\text{OH})_3$ was purer than the limiting stage. The two results are summarised in the following table.

TABLE XI

Concentration of Weiser's sol = 6.46 g./litre.	Concentration of author's sol = 9.018 g./litre.
Chlorine content = 0.0158 g. ions/litre.	Chlorine content = 0.012 g. ions/litre.
Purity of Weiser's sol = 408.7,	Purity of author's sol = 751.0.

Electrolytes used.	Displacement of $[Cl] \times 10^5$ from sol used by Weiser.	Displacement of $[Cl] \times 10^5$ from sol used by author.
KNO ₃
KIO ₃	...	1.72
K ₂ SO ₄	4.67	4.05
K-citrate	4.10	2.86
K ₃ Fe(CN) ₆	3.17	...

From the results recorded in Tables IV-IX, the following tables have been calculated in which the release of chlorine ions as observed and calculated when adding one electrolyte in presence of another is given. The theoretical release due to the combined effect of both the electrolytes has also been calculated and given in columns 2 and 5 of the following tables.

TABLE XII

Displacement of chlorine ions from Fe(OH)₃ sol when N/50-K₂SO₄ + N/10-KIO₃ and N/200-K-citrate + N/10-KIO₃ are added to it in pairs.

0.5 c.c. K ₂ SO ₄ + c.c. of KIO ₃ .	Calc.	Obs.	1 c.c. K-citr. + c.c. of KIO ₃ .	Calc.	Obs.	$[Cl]$ eqvt. to electro- lyte added.
0.25	0.80	0.52	0.25	0.28	0.39	3.50
0.50	0.81	0.95	0.50	0.39	0.68	6.00
1.00	1.22	1.50	1.00	0.70	0.82	11.00
1.50	1.45	1.98	1.50	0.93	1.30	16.00
1.75	1.60	2.34	18.50
2.00	2.70	2.63	2.00	1.20	1.50	21.00
2.50	2.50	1.50	2.51	26.00

TABLE XIII

Displacement of chlorine ions from $\text{Fe}(\text{OH})_3$ sol when $N/10\text{-KIO}_3 + N/50\text{-K}_2\text{SO}_4$ and $N/10\text{-KIO}_3 + N/200\text{-K-citrate}$ are added in pairs to it.

1 c.c. $\text{KIO}_3 +$ c.c. of K_2SO_4 .	Calc.	Obs.	1 c.c. $\text{KIO}_3 +$ c.c. K-citr.	Calc.	Obs.	[Cl] eqvt. to electro- lyte added $\times 10^3$.
0.10	0.67	0.66	10.20
...	0.25	0.62	0.78	10.26
0.20	0.82	1.89	10.40
...	0.50	0.70	1.57	10.50
0.40	1.04	2.05	10.80
...	1.00	0.85	1.77	11.00
0.60	1.32	2.83	11.20
...	1.25	0.97	2.07	11.25
...	1.50	1.09	2.65	11.50
0.80	1.62	3.90	11.80
1.00	1.83	5.86	2.00	1.67	2.93	12.00

TABLE XIV

Displacement of chlorine ions from $\text{Fe}(\text{OH})_3$ sol when $N/200\text{-K-citrate} + N/50\text{-K}_2\text{SO}_4$ and $N/50\text{-K}_2\text{SO}_4 + N/200\text{-K-citrate}$ are added in pairs to it.

1 c.c. K-citr. + c.c. K_2SO_4	Calc.	Obs.	1 c.c. $\text{K}_2\text{SO}_4 +$ c.c. K-citr.	Calc.	Obs.	[Cl] eqvt. to electro- lyte added $\times 10^3$.
0.10	0.25	0.18	1.20
0.30	0.50	0.31	1.60
0.60	0.90	0.71	2.20
...	0.25	0.80	0.60	2.25
...	0.50	0.88	1.04	2.50
0.90	1.27	1.23	2.80
1.00	3.77	3.32	1.00	1.03	1.25	3.00
...	1.25	1.12	1.44	3.25
1.20	1.55	1.87	3.40
...	1.50	1.27	1.55	3.50
1.50	0.71	2.82	2.00	1.75	1.97	4.00

From the above results we find that with ferric hydroxide sol, in almost all cases, amount of released chlorine is greater than the calculated value. This means that the mixture induces more instability than the combined effects of the two electrolytes when taken in singles. A necessary consequence of this is that there should be no positive ionic antagonism *i.e.*, the amount of electrolyte necessary to coagulate should be less than than the additive. This has been observed by previous workers with these sols but with other pairs of electrolytes.