

STUDIES ON THE ELECTROCHEMICAL PREPARATION OF SODIUM HYDROSULPHITE.

PART IV. ELECTROCHEMICAL PRODUCTION OF SOLID HYDROSULPHITE

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In our previous publication (Patel and Rao, 1949) on the direct electrochemical preparation of sodium hydrosulphite by the reduction of bisulphite, the maximum concentration of hydrosulphite obtained in the cathode solution was 10.7%, which was much higher than that obtained by earlier workers (K. Jellinek and E. Jellinek, 1919). Attempts to raise this value, however, were unsuccessful owing to the decomposition of hydrosulphite at higher concentration. In order to prevent the decomposition of hydrosulphite, it was necessary to keep down the effective concentration of the sodium hydrosulphite in the catholyte. This could be effected by the precipitation of hydrosulphite (1) by the conversion of the hydrosulphite produced into an insoluble form like calcium hydrosulphite, and (2) by crystallisation as $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ by the addition of sodium chloride to take advantage of the common ion effect. When calcium chloride was added to the catholyte, the hydrosulphite was precipitated as its calcium salt and the total concentration of the hydrosulphite went beyond 13% on prolonged electrolysis. The precipitate was found to contain about 37% of calcium hydrosulphite, the rest being calcium sulphite. Although by this method one could succeed in getting a higher concentration of hydrosulphite, yet the contamination of the calcium hydrosulphite by the calcium sulphite was the main disadvantage. Hence, this method was not continued further.

On the other hand, when sodium chloride was added to the catholyte, preliminary experiments indicated that the total concentration of hydrosulphite went beyond 13%, precipitating at the same time pure sodium hydrosulphite in the catholyte. Hence, this method was investigated in detail.

EXPERIMENTAL.

The apparatus, used in the investigation for the electrochemical preparation of sodium hydrosulphite was essentially the same as that employed by the authors described in a previous publication (Patel and Rao, 1949). The following are the modifications (Fig. 1) effected in order to get a quantitative idea of the various products of reaction. (1) In the earlier work, the solution for analysis was directly drawn into the burette but this was not practicable in the present case due to the formation of the hydrosulphite slurry in the catholyte. The cathode slurry was therefore, pipetted out for analysis of hydrosulphite through an opening *H* which was normally kept closed by a glass rod. (2) The cathode chamber was provided with a fritted glass filter *F*, connected to the microburette *B*. The arrangement indicated in the diagram enabled one to remove the filtered catholyte for analysis by using suction. (3) An inlet for sulphur dioxide was also provided as shown in the figure. (4) The external surface of the porous diaphragm *D*, above the level of

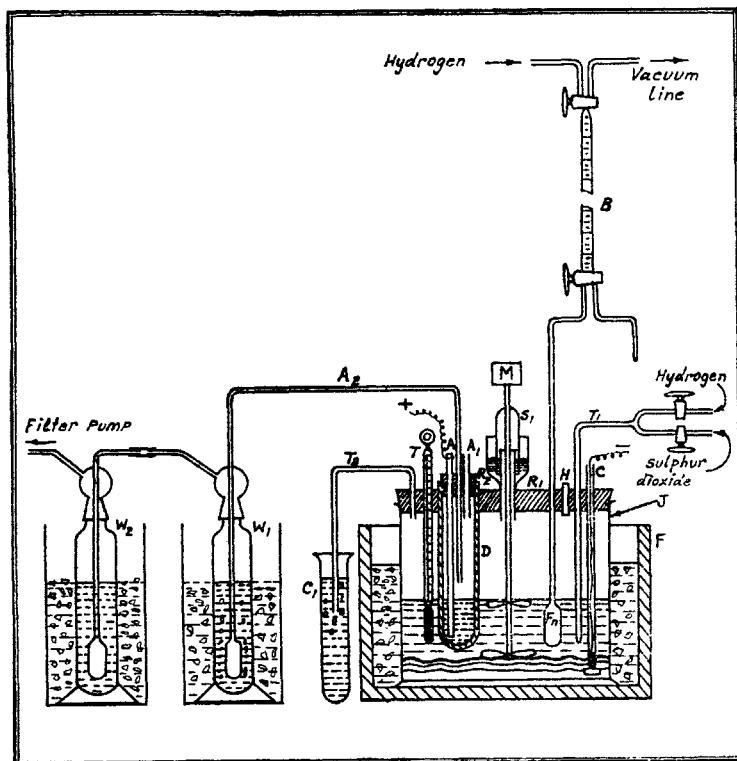


FIG. 1.— A_1 = Inlet tube for air, A_2 = outlet tube for gases, S_1 = mercury seal stirrer, J = glass jar, F = water bath, T_1 = gas inlet tube, T_2 = exit gas tube, C_1 = water seal, C = connecting tube for mercury cathode, R_1 & R_2 = Rubber Stoppers.

the liquid, was coated with paraffin to prevent the escape of anode gases into the cathode compartment. The diaphragm, serving as anode chamber, was closed at the top with a paraffined rubber stopper R_2 provided with two glass tubes as in the figure. The gases produced in the anode chamber were swept into the gas washing bottles W_1 and W_2 containing caustic alkali. The anode A consisted of a graphite rod in place of a platinum electrode used in the earlier work.

MATERIALS EMPLOYED.

(1) *Sodium bisulphite solution*.—A stock solution of bisulphite was prepared in an inert atmosphere by passing sulphur dioxide through aqueous sodium carbonate (c.p.), employing an external indicator (methyl yellow screened with methylene blue) which turned pink at pH 4.3. The solution thus prepared was analysed for its bisulphite content and preserved under an inert atmosphere. The bisulphite solution was free from sulphate.

(2) Standard analytical solutions used in this investigation were generally prepared from chemicals of A.R. quality. The rest of the chemicals employed were of C.P. grade.

(3) *Sulphur dioxide*.—It was taken from a cylinder containing liquid sulphur dioxide and was found to be free from oxygen.

(4) *Hydrogen*.—It was electrolytically prepared and was freed from any oxygen by passing through alkaline pyrogallol.

METHODS OF ANALYSIS.

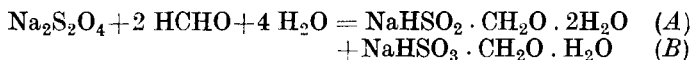
(a) Estimation of Hydrosulphite.

50 ml. of dilute air-free ammonia was added to a definite volume of standard cuprammonium sulphate solution in a glass cylinder and the mixture was covered with a layer of benzene, 1 cm. thick, to prevent atmospheric oxidation of hydrosulphite. 2.0 ml. of the well stirred catholyte was pipetted out (maintaining an inert atmosphere in the pipette) into the mixture with good stirring. The excess of the hydrosulphite was estimated by the addition of the standard cuprammonium sulphate solution as described by the authors in a previous publication (Patel and Rao, 1949).

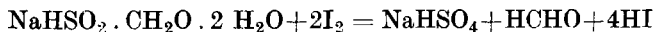
(b) Estimation of thiosulphate in presence of hydrosulphite.

This method is based in principle on Merriman's method (1923) for the estimation of hydrosulphite.

One ml. of the filtered catholyte from the microburette was delivered into 30 ml. of air-free aqueous sodium hydroxide (1%) containing 5 ml. of 40% formaldehyde and the contents were mixed well and kept for 20 minutes. The solution was then neutralised with 20% acetic acid. Excess of standard iodine solution was added and the excess was titrated against standard thiosulphate solution. The iodine consumed above corresponds to hydrosulphite and thiosulphate, and as the hydrosulphite value is already known, the thiosulphate can be calculated. Any bisulphite present in the solution is bound by the formaldehyde and does not react with iodine. The hydrosulphite reacts with formaldehyde as follows:

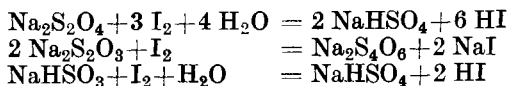


The iodine does not react with the bisulphite complex (B), while the sulphoylate complex (A) is acted upon according to the following reaction:

*(c) Estimation of sodium bisulphite in presence of hydrosulphite and thiosulphate.*

This process was used by Wollak (1930) for the estimation of sulphite, when the values for hydrosulphite and thiosulphate present in the mixture were known.

One ml. of the filtered catholyte was added to excess of standard iodine solution together with 50 ml. of air-free distilled water containing 1 g. of sodium acetate to neutralise the acid formed during the reaction. The excess of iodine was titrated against thiosulphate. The reactions involved are:



As the hydrosulphite and thiosulphate values are already known, the sulphite content can easily be calculated.

(d) Estimation of sodium chloride and 'total sulphur'.

The estimation of chloride and 'total sulphur' could not be carried out in presence of hydrosulphite, bisulphite and thiosulphate. Hence the solution had to be oxidised to convert all the sulphur compounds into the sulphate by the procedure employed by Harnist (1921). 1.0 ml. of the filtered catholyte was introduced into a 250 ml. pyrex conical flask containing 30 ml. of 1% sodium hydroxide solution. 1 g. of sodium peroxide (free from chloride and sulphate) was

added to it. The flask was shaken carefully and then heated on a water bath for about half an hour to complete the oxidation. The contents of the flask were cooled and made up to 100 ml. Aliquots were employed for the analysis of the chloride and the sulphate. The chloride was estimated volumetrically by Volhard's method and the sulphate gravimetrically as barium sulphate.

(e) *Estimation of total hydrosulphite produced during the electrolytic reduction.*

After the electrolysis, the current was switched off. The catholyte was made alkaline by addition of dilute ammonia and the hydrosulphite was completely brought into solution by addition of sufficient air-free water at 0°C. A sample was withdrawn and the hydrosulphite was determined by the cuprammonium sulphate method. The total volume of the diluted cathode solution was then measured. The total hydrosulphite produced could thus be computed with suitable corrections for the samples withdrawn at intervals for analysis and the overall current efficiency calculated.

(f) *Estimation of chlorine.*

The chlorine produced at the anode was absorbed in sodium hydroxide cooled in ice. The hypochlorite formed was estimated by acidified potassium iodide method.

TABLE I.

*Electrochemical preparation of Sodium hydrosulphite.
Effect of addition of Sodium chloride to the catholyte.*

Current density at the cathode: 2.16 amp./dm.²

Catholyte: 100 ml. aqueous solution containing 30 g. sodium bisulphite and 10 g. sodium chloride.

Anolyte: 10 ml. saturated solution of sodium bicarbonate.

Current passed: 0.8 amp. Temperature: 8°C.

Potential difference: 4 to 5 volts.

Time in hours	Na ₂ S ₂ O ₄ in catholyte. %	Total Na ₂ S ₂ O ₄ formed.* g.	Approximate current efficiency. %
1	2.44	2.44	94.1
2.5	5.68	5.61	86.5
3	6.45 (crystals)	6.35	81.5
4	8.11	7.89	76.0
5	10.35	9.92	76.4
6	11.14	10.60	68.1
7	12.48	11.72	64.5
8	13.63	12.67	61.0
9	12.12	Decomposition	..

* In analysing the catholyte periodically, some solution was removed and with it some hydrosulphite. In arriving at the figures in this column, the hydrosulphite thus removed has been duly taken into account.

Procedure for the electrochemical preparation of hydrosulphite:

Into the electrolytic cell were placed 60 ml. of purified mercury and 100 ml. of an aqueous solution containing 30% sodium bisulphite and 10% sodium chloride. All the air in the cathode chamber had been displaced by purified hydrogen. The temperature of the catholyte was lowered to 8°C. A saturated solution (10 ml.) of sodium bicarbonate was used as anolyte. The stirrer S_1 was set in motion and the current from the D.C. mains was switched on. The current, which was measured by a calibrated ammeter, could be kept constant with the aid of a rheostat. The voltage between the two terminals of the cell was noted by means of an accurate voltmeter. The concentration of hydrosulphite increased with the passage of the current and when the concentration was about 6%, crystals of hydrosulphite were formed. The slurry of the hydrosulphite crystals thus formed was analysed from time to time. The results obtained are given in Table I.

The results (Table I) indicate that the highest concentration of sodium hydrosulphite obtained in the cathode slurry is 13.6% as against 10.7% obtained in the previous work (Patel and Rao, 1949). It is further seen that the current efficiency gradually falls from 94% to 61% during the course of 8 hours, showing that the rate of formation of sodium hydrosulphite gradually drops off and towards the end it has become even negative.

On examination of the catholyte at the end of the experiment, it was found that the solution was slightly alkaline. According to the investigations of Patel and Rao (1949) the optimum pH for the maximum formation of sodium hydrosulphite by the electrochemical reduction of sodium bisulphite is between 5 and

TABLE II.

Effect of sulphur dioxide on hydrosulphite production.

Current density at the mercury cathode: 2.16 amp./dm.²

Catholyte: 100 ml. aqueous solution containing 30 g. sodium bisulphite and 10 g. sodium chloride.

Anolyte: 10 ml. of saturated solution of sodium bicarbonate.

Current passed: 0.8 amp. P.D. = 4 to 5 volts.

pH of the cathode solution: about 5.

Temperature: 8°C.

Time in hours.	SO ₂ passed. g.	Na ₂ S ₂ O ₄ in catholyte. %	Total Na ₂ S ₂ O ₄ formed. g.	Approximate current efficiency. %
1	1.04	2.41	2.41	92.7
2	1.38	4.43	4.39	84.7
3	1.04	6.02	5.91	75.8
4	0.69	7.52 (crystals)	7.30	70.3
5	0.35	9.37	8.97	69.0
6	0.69	11.03	10.48	67.3
7	0.69	13.08	12.27	67.5
8	0.69	15.20	13.98	67.3
9	0.35	15.93	14.58	62.4

5.5. In order to maintain the pH near the optimum value, the alkali produced in the catholyte was carefully neutralised by passing a measured amount of pure sulphur dioxide. Excess of sulphur dioxide passed could be detected by the formation of brown hydrosulphurous acid (dithionous acid, $H_2S_2O_4$) in the catholyte. The results obtained are given in Table II.

The results (Table II) indicate that the concentration of sodium hydrosulphite in the cathode slurry could be increased to 15.9% by maintaining the pH at about 5 by the passage of sulphur dioxide into the catholyte. There was a marked improvement in the current efficiency. The results were found to be reproducible.

In order to reduce the solubility of hydrosulphite still further, the concentration of sodium chloride in the catholyte was raised to 20%. Sulphur dioxide was bubbled into the catholyte as in the previous experiment to control the pH . Results obtained are given in Table III.

TABLE III.

Effect of increased concentration of sodium chloride (20%) on hydrosulphite production.

Current Density at the mercury cathode: 2.16 amp./dm.²

Catholyte: 100 ml. aqueous solution containing 27.4 g. sodium bisulphite and 20 g. sodium chloride.

Anolyte: 10 ml. saturated solution of sodium bicarbonate.

Current passed: 0.8 amp. P.D.: 4 to 5 volts.

Temperature: 8°C.

Time in hours.	SO ₂ passed. g.	Na ₂ S ₂ O ₄ in catholyte. %	Total Na ₂ S ₂ O ₄ formed. g.	Approximate current efficiency. %
1	1.38	2.42	2.42	93.2
2	1.38	4.49	4.44	85.5
3	1.38	6.81 (crystals)	6.66	85.5
4	1.04	8.79	8.51	80.0
5	0.69	10.99	10.53	81.1
6	0.69	12.83	12.18	78.2
7	0.35	14.92	14.02	77.1
8	0.69	16.99	15.83	76.2
9	0.35	18.91	17.44	74.6

The above results indicate that the concentration of sodium hydrosulphite in the cathode slurry is increased to 18.9% by increasing the concentration of sodium chloride to 20%. Increase in concentration of sodium chloride is also found to yield higher current efficiency.

A study of Tables II and III shows that crystallisation of hydrosulphite starts in the catholyte at the hydrosulphite concentrations of 6% and 3% when the corresponding strengths of sodium chloride are 10% and 20% respectively. The sodium chloride in the catholyte has, therefore, a marked effect on hydrosulphite solubility.

The experiments described above clearly indicate that an increased production of sodium hydrosulphite could be obtained when the hydrosulphite is crystallised in the catholyte. To determine the optimum conditions for the production of the hydrosulphite, the following aspects were studied in detail: (1) composition of anolyte, (2) composition of catholyte, (3) effect of temperature, and (4) effect of current density. In all these cases the catholyte was quantitatively analysed for hydrosulphite, bisulphite, thiosulphate, etc. The overall current efficiency was also calculated by the estimation of the total hydrosulphite as described already.

Composition of the anolyte.

In the previous experiments sodium bicarbonate was employed as anolyte. Since the solubility of the bicarbonate is small (about 8%), the cell resistance was high. In order to reduce the cell resistance, sodium bicarbonate solution was replaced by (1) the cathode solution containing sodium bisulphite and sodium chloride, (2) cathode solution containing an excess (suspension) of sodium chloride and (3) aqueous sodium chloride having suspension of solid sodium chloride.

TABLE IV.

Effect of employing aqueous solution of sodium bisulphite and sodium chloride for both anolyte and catholyte.

Current density at the cathode: 2.05 amp./dm.²
 Catholyte: 120 ml. aqueous solution containing 28.46% sodium bisulphite and 18.37% sodium chloride.
 Anolyte: 10 ml. solution of the same composition as catholyte. Current passed: 0.76 amp.
 Cathode: Mercury. Anode: Graphite. Temperature: 5°C. P.D.: 4 to 4.5 volts.

Time in hours.	SO ₂ passed. g./hr.	Composition of filtered catholyte. g. in 100 ml. soln.				Na ₂ S ₂ O ₄ in 100 ml. slurry. g.	Total production in g.		Current efficiency in %	
		Na ₂ S ₂ O ₄	Na ₂ S ₂ O ₃	NaHSO ₃	NaCl		Na ₂ S ₂ O ₄	Cl ₂	Na ₂ S ₂ O ₄	Cl ₂
1	0.35	2.000	..	26.79	17.35	..	2.41	nil	97.6	0.0
2	2.41	2.115	..	26.40	17.09	3.58	4.17	0.27	84.5	13.2
3	1.21	2.060	..	25.95	16.80	5.62	6.30	0.94	85.1	31.2
4	1.38	2.060	..	23.86	16.19	7.47	8.02	1.41	81.3	35.0
5	0.52	2.115	..	23.22	15.53	9.18	9.39	1.74	76.2	34.6
6	1.04	2.115	..	22.57	15.26	11.18	10.86	1.96	73.4	32.4
						(Overall values)→	(11.79)		(79.7)	

The results in Table IV show that the current efficiency for hydrosulphite is quite high (79.7%) while that for chlorine is very low (32.4%). No thiosulphate is formed in the catholyte.

It was noticed during the later stages of electrolysis that a brown ring of hydrosulphurous acid (H₂S₂O₄) was formed in the catholyte around the diaphragm. Evidently, the bisulphite in the anolyte was oxidised by chlorine and sulphuric acid was formed. The acid thus formed diffused around the diaphragm producing hydrosulphurous acid at the diaphragm in the catholyte.

In order to reduce the solubility of chlorine in the anolyte, solid sodium chloride was kept in suspension in the anolyte and the effect on the preparation of hydrosulphite and chlorine was studied. The results obtained are given in Table V.

TABLE V.

*Effect of addition of solid sodium chloride to the anolyte.*Current density at the cathode: 2.05 amp./dm.²

Catholyte: 120 ml. aqueous solution containing 28.03% sodium bisulphite and 19.30% sodium chloride.

Anolyte: 10 ml. cathode solution + 6 g. solid sodium chloride. Current passed: 0.76 amp. Cathode: Mercury. Anode: Graphite. Temperature: 5°C. P.D.: 4 to 4.5 volts.

Time in hours.	SO ₂ passed. g./hr.	Composition of filtered catholyte, g. in 100 ml. soln.				Na ₂ S ₂ O ₄ in 100 ml. slurry. g.	Total production in g.		Current efficiency in %	
		Na ₂ S ₂ O ₄	Na ₂ S ₂ O ₃	NaHSO ₃	NaCl		Na ₂ S ₂ O ₄	Cl ₂	Na ₂ S ₂ O ₄	Cl ₂
1	1.04	2.00	..	25.89	18.52	..	2.41	..	97.6	..
2	1.38	3.339	..	25.37	18.04	3.47	4.09	..	82.9	..
3	1.21	2.449	..	24.44	17.54	5.57	6.42	..	86.8	..
4	1.55	2.393	..	24.04	16.96	7.47	8.32	..	84.3	..
5	1.04	2.393	..	23.87	16.43	9.48	10.16	..	82.3	..
6	0.69	2.449	..	23.18	15.72	12.53	12.83	4.89	86.7	81.1
						(Overall values)→(12.68)		(85.7)		

The results (Table V) indicate that the current efficiency for the production of hydrosulphite and chlorine is 85% and 81% respectively. Thus the addition of solid sodium chloride to the anolyte helped to increase the current efficiency for chlorine.

In subsequent experiments, the anolyte consisted of a saturated solution of sodium chloride containing an excess of the solid. Solid sodium chloride was also added (in suspension) to the catholyte in order to replenish the salt that got consumed during electrolysis. It was found during this experiment that crystals of hydrosulphite were formed during the first hour itself. The results obtained are given in Table VI.

TABLE VI.

*Effect of addition of solid sodium chloride in both the catholyte and the anolyte, the latter having no bisulphite.*Current density at the cathode: 2.05 amp./dm.²

Catholyte: 120 ml. aqueous solution containing 32.42 g. sodium bisulphite. 35 g. solid sodium chloride was added to it. The expanded volume on addition of sodium chloride was 131 ml.

Anolyte: 10 g. sodium chloride + 10 ml. water. Current passed: 0.76 amp.

Cathode: Mercury. Anode: Graphite. Temperature: 5°C. P.D.: 4 to 4.5 volts.)

Time in hours.	SO ₂ passed. g./hr.	Composition of filtered catholyte, g. in 100 ml. soln.				Na ₂ S ₂ O ₄ in 100 ml. slurry. g.	Total production in g.		Current efficiency in %	
		Na ₂ S ₂ O ₄	Na ₂ S ₂ O ₃	NaHSO ₃	NaCl		Na ₂ S ₂ O ₄	Cl ₂	Na ₂ S ₂ O ₄	Cl ₂
1	1.38	1.781	..	21.9	22.9	1.787	2.34	0.89	94.8	88.7
2	2.07	1.781	..	22.7	23.2	3.473	4.46	1.84	90.4	91.6
3	1.73	1.614	..	22.7	23.1	4.920	6.02	2.77	81.3	91.7
4	1.21	1.603	..	20.9	23.2	7.108	8.56	3.74	86.8	92.9
5	1.55	1.447	..	21.7	23.1	9.378	10.87	4.60	88.1	91.4
6	1.04	1.592	..	21.0	22.6	11.540	12.87	5.52	87.0	91.4
						(Overall values)→(13.41)		(90.6)		

The results (Table VI) indicate that the addition of solid sodium chloride to the catholyte lowers the solubility of hydrosulphite from about 2.4% (Table V) to 1.6%. The concentration of bisulphite and chloride in the filtered catholyte remains almost constant throughout the experiment. The current efficiencies for the production of hydrosulphite and chlorine are appreciably enhanced and are nearly of the same order (91%) for both the products. No thiosulphate is noticed in the catholyte.

The results of analysis of sulphur compounds in the filtered catholyte of the above experiment are given in Table VII.

TABLE VII.
Sulphur compounds in the catholyte.

Time in hours.	G-atoms of Sulphur $\times 10^2$				(e) Sulphur in G-Atoms estimated as sulphate $\times 10^2$	(e) - (d)
	(a) $\text{Na}_2\text{S}_2\text{O}_4$	(b) NaHSO_3	(c) $\text{Na}_2\text{S}_2\text{O}_3$	(d) Total (a + b + c)		
1	2.68	27.56	..	30.24	30.93	0.69
2	2.58	27.49	..	30.07	30.29	0.22
3	2.25	26.40	..	28.65	28.93	0.28
5	1.85	23.11	..	24.96	26.31	1.35
6	1.94	21.27	..	23.21	24.57	1.36

It would be noticed from the above table, that the two values for total sulphur agree well, except at the later stages of electrolysis, when diffusion of anolyte into the cathode chamber is likely to be a disturbing influence.

Effect of bisulphite concentration on the production of hydrosulphite.

To study the effect of concentration of the bisulphite, an experiment was conducted in which bisulphite strength was reduced to 8.6%. The results are recorded in Table VIII.

TABLE VIII.
Effect of lower concentration of sodium bisulphite in the catholyte on the production of hydrosulphite.

Current density at the cathode: 2.05 amp./dm.²
 Catholyte: 120 ml. aqueous solution containing 11.27 g. sodium bisulphite. 30 g. of solid sodium chloride was added to it. The expanded volume on addition of sodium chloride was 131 ml.
 Anolyte: 10 g. sodium chloride + 10 ml. water. Current passed: 0.76 amp.
 Cathode: Mercury. Anode: Graphite. Temperature: 5°C. P.D.: 5 volts.

Time in hours.	SO_2 passed, g./hr.	Composition of filtered catholyte, g. in 100 ml. soln.				$\text{Na}_2\text{S}_2\text{O}_4$ in 100 ml. slurry, g.	Total production in g.		Current efficiency in %	
		$\text{Na}_2\text{S}_2\text{O}_4$	$\text{Na}_2\text{S}_2\text{O}_3$	NaHSO_3	NaCl		$\text{Na}_2\text{S}_2\text{O}_4$	Cl_2	$\text{Na}_2\text{S}_2\text{O}_4$	Cl_2
1	1.38	1.837	..	8.45	22.1	..	2.41	0.89	97.6	88.5
2	1.38	3.562	..	7.33	21.6	..	4.60	1.82	93.2	90.5
3	1.73	2.949	..	7.83	20.7	5.17	6.57	2.75	88.8	90.9
4	1.38	2.895	0.358	7.68	20.1	6.68	8.27	3.70	83.8	91.8
5	1.38	3.006	0.469	7.19	19.9	8.80	10.53	4.63	85.4	92.0
6	1.38	2.973	0.591	7.01	18.7	10.42	12.06	5.57	81.5	92.1
(Overall values) →						(12.52)			(84.6)	

The results of the above table show that the current efficiency for hydrosulphite is lowered from 90.6% (Table VI) to 84.6%. It is to be noted that a small quantity of thiosulphate is produced in the catholyte. This is probably due to the reduction of the hydrosulphite as described later.

The results of analysis of various sulphur compounds of the filtered catholyte drawn out periodically during the above experiment are given in Table IX.

TABLE IX.
Sulphur compounds in the catholyte.

Time in hours.	G-atoms of Sulphur $\times 10^2$				(c) Sulphur in G-Atoms estimated as sulphate $\times 10^2$	(c) - (d)
	(a) $\text{Na}_2\text{S}_2\text{O}_4$	(b) NaHSO_3	(c) $\text{Na}_2\text{S}_2\text{O}_3$	(d) Total (a+b+c)		
0	..	10.83	..	10.83	10.96	0.13
1	2.77	10.64	..	13.41	13.58	0.17
2	5.20	8.95	..	14.15	14.35	0.20
3	4.17	8.67	..	12.84	13.11	0.27
4	3.93	8.71	0.53	13.17	13.49	0.32
5	3.90	7.81	0.67	12.38	12.61	0.23
6	3.69	7.28	0.82	11.79	12.13	0.34

It would be noticed from the above results that hydrosulphite, sulphite and thiosulphate seem to be the only three sulphur compounds in solution.

Effect of temperature of electrolysis on the production of hydrosulphite.

In this case, the bisulphite concentration of the catholyte was kept at 25.4% and an excess of solid sodium chloride was maintained in the catholyte. The

TABLE X.

Effect of room temperature on electrochemical preparation of hydrosulphite.

Current density at the cathode: 2.05 amp./dm.²

Catholyte: 120 ml. aqueous solution containing 33.50 g. of sodium bisulphite. 35 g. solid sodium chloride was added to it. The expanded volume on addition of sodium chloride was 132 ml.

Anolyte: 10 g. sodium chloride + 10 ml. water. Current passed: 0.76 amp.

Cathode: Mercury. Anode: Graphite. Temperature: 21°C. \pm 0.5°C. P.D.: 4 to 4.5 volts.

Time in hours.	SO_2 passed. g./hr.	Composition of filtered catholyte, g. in 100 ml. soln.				$\text{Na}_2\text{S}_2\text{O}_4$ in 100 ml. slurry. g.	Total production in g.		Current efficiency in %	
		$\text{Na}_2\text{S}_2\text{O}_4$	$\text{Na}_2\text{S}_2\text{O}_3$	NaHSO_3	NaCl		$\text{Na}_2\text{S}_2\text{O}_4^*$	Cl_2	$\text{Na}_2\text{S}_2\text{O}_4$	Cl_2
1	0.69	1.447	..	23.9	22.7	..	1.91	0.86	77.5	85.3
2	0.94	1.954	0.37	21.7	22.6	2.372	3.07	1.82	62.2	90.6
3	1.21	1.865	0.83	19.8	22.5	3.380	4.22	2.70	57.0	89.3
4	1.38	1.726	1.20	20.4	22.4	4.028	4.82	3.62	48.9	89.9
5	0.72	1.714	1.86	18.7	22.4	5.222	5.86	4.48	47.5	88.9
6	0.60	1.865	2.04	16.3	21.5	6.412	6.62	5.41	44.8	89.6
						(Overall values) \rightarrow	(9.95)		(67.2)	

*In spite of stirring, uniform slurry of hydrosulphite crystals could not be obtained at room temperature as the crystals were settling down, and hence the appreciable difference in the overall current efficiency and the current efficiency at the end of six hours.

electrolysis was carried out at room temperature. Formation of crystals of hydrosulphite was noticed during the second hour of electrolysis. The results are recorded in Table X.

The results (Table X) show that the overall current efficiency for hydrosulphite dropped down to 67.2% as compared with 90.6% at 5° C. (Table VI). Added to this, considerable quantities of thiosulphate are produced in this case.

Effect of Current Density on the Production of Hydrosulphite.

Experiments were conducted with the current densities of 3.62 and 5.11 amp./dm², and the results are given in Tables XI and XII.

TABLE XI.

Effect of current density on the production of hydrosulphite, current density at the cathode being 3.62 amp./dm.²

Catholyte: 120 ml. aqueous solution containing 35.1 g. NaHSO₃. 35 g. solid sodium chloride was added to it. The expanded volume on addition of sodium chloride was 131 ml.

Anolyte: 10 g. sodium chloride + 10 ml. water. Current passed: 1.34 amp.

Cathode: Mercury. Anode: Graphite. Temperature: 5° C. ± 0.5° C. P.D.: 7 to 7.2 volts.

Time in hours.	SO ₂ passed. g./hr.	Composition of filtered catholyte, g. in 100 ml. soln.				Na ₂ S ₂ O ₄ in 100 ml. slurry. g.	Total production in g.		Current efficiency in %	
		Na ₂ S ₂ O ₄	Na ₂ S ₂ O ₃	NaHSO ₃	NaCl		Na ₂ S ₂ O ₄	Cl ₂	Na ₂ S ₂ O ₄	Cl ₂
1	2.07	2.226	..	23.9	21.2	3.03	4.06	1.39	91.3	78.4
2	1.73	1.837	..	22.5	21.7	6.32	8.04	2.93	92.5	82.6
3	2.07	1.971	..	21.6	21.7	9.45	11.53	4.46	88.4	83.8
4	1.73	1.519	0.495	20.9	21.3	11.97	13.93	5.95	81.0	83.8
5	2.42	1.737	0.547	21.7	20.4	14.58	16.16	7.08	74.3	79.8
6	0.69	1.447	1.525	19.2	19.9	16.80	17.69	8.17	67.8	76.7
						(Overall values) →	(19.62)		(75.2)	

TABLE XII.

Effect of current density on the production of hydrosulphite, current density at the cathode being 5.11 amp./dm.²

Catholyte: 120 ml. aqueous solution containing 36.31 g. sodium bisulphite. 35 g. solid sodium chloride was added to it. The expanded volume on addition of sodium chloride was 131 ml.

Anolyte: 10 g. sodium chloride + 10 ml. water. Current Passed: 1.89 amp.

Cathode: Mercury. Anode: Graphite. Temperature: 5° C. ± 1° C. P.D.: 7 to 7.8 volts.

Time in hours.	SO ₂ passed. g./hr.	Composition of filtered catholyte, g. in 100 ml. soln.				Na ₂ S ₂ O ₄ in 100 ml. slurry. g.	Total production in g.		Current efficiency in %	
		Na ₂ S ₂ O ₄	Na ₂ S ₂ O ₃	NaHSO ₃	NaCl		Na ₂ S ₂ O ₄	Cl ₂	Na ₂ S ₂ O ₄	Cl ₂
1	2.07	1.892	..	24.9	21.4	4.25	5.56	2.09	90.6	83.6
2	1.73	1.670	..	23.0	21.2	7.49	9.54	4.26	77.8	85.1
3	3.11	1.697	0.061	22.7	20.4	10.78	13.27	5.98	72.1	79.6
4	2.76	1.692	1.412	22.1	18.0	12.87	14.97	7.80	61.0	78.0
5	1.73	1.781	2.713	19.1	17.9	14.33	15.81	9.54	51.4	76.3
6	1.73	1.614	5.163	18.5	17.0	10.76	..	71.6
						(Overall values) →	(18.94)		(61.5)	

A reference to these tables indicates that the current efficiencies for the production of hydrosulphite is quite high initially, but the value is diminished considerably towards the end of the experiment. The overall current efficiency for hydrosulphite is 75.2% (Table XI) and 51.5% (Table XII) and for chlorine 76.6% and 71.6% respectively. It has to be pointed out that at higher current density, thiosulphate production increased considerably, the final solution (catholyte) having 5.2% of the thiosulphate in solution (Table XII). It can, therefore, be concluded that low current density is advantageous for the production of hydrosulphite.

Maintaining a current density of 2.05 amp./dm.² continuous electrolysis was carried out for a period of 14 hours under the experimental conditions described in Table VI. The overall current efficiency for hydrosulphite was 82.5%, with a total amount of hydrosulphite produced being 28.5 g. Due to large accumulation of solid hydrosulphite in the catholyte, stirring was considerably ineffective and this facilitated the secondary reactions. It is desirable that experiments of long duration could be more successful if the hydrosulphite crystals are removed from the catholyte at frequent intervals. The chlorine evolved at the anode was 12.0 g. with a current efficiency of 84.9%.

DISCUSSION.

As has already been pointed out, attempts by other workers to obtain hydrosulphite by a direct electrochemical method were unsuccessful owing to the decomposition of hydrosulphite in the catholyte. The preparation of hydrosulphite crystals by the direct electrochemical method was successful in this investigation on account of the addition of sodium chloride to the catholyte. In presence of sodium chloride, the hydrosulphite was salted out before its concentration reached a high value, at which the hydrosulphite suffered decomposition at the cathode. Addition of sodium chloride was also found to increase the current efficiency of the electrochemical process due to the maintenance of lower effective concentration of hydrosulphite in the catholyte.

Data presented in Tables II and III indicate that the current efficiency for the production of sodium hydrosulphite was only 62.4%, when 10% sodium chloride was present in the catholyte; whereas the current efficiency rose to 74.6% when the chloride concentration was raised to 20% in the catholyte, other experimental conditions being practically the same. When suspension of the salt was present in both the catholyte and anolyte, the current efficiency rose to 90% (Table VI). This indicates that the concentration of sodium chloride in the catholyte should be as high as possible for the maximum yield of hydrosulphite. In the preparation of pure sodium hydrosulphite crystals, the suspension of sodium chloride should be avoided and the concentration of the sodium chloride should be maintained slightly below that of the saturation value (20%).

The addition of sodium chloride to the catholyte offers certain other advantages. The chloride acts as a cheap source for the sodium amalgam. It also considerably increases the conductivity of the electrolyte. When bisulphite alone was used as the catholyte, the voltage of the cell varied between 6 and 8 volts. On adding sodium chloride to the electrolyte the voltage, however, dropped to 4 to 5 volts, the diaphragm and the current density being the same in the two cases.

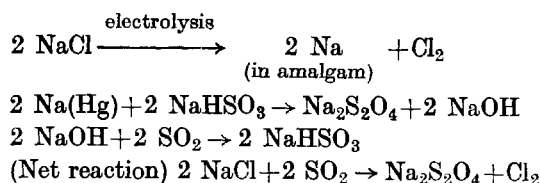
Data presented in Tables I to III indicate that the passage of sulphur dioxide into the catholyte is essential for the continuous production of sodium hydrosulphite. When sulphur dioxide is not introduced, the rate of production of hydrosulphite is slowly reduced and at a certain stage, actually more hydrosulphite is decomposed than can be produced in unit time (Table I). When sulphur dioxide is continuously supplied to the catholyte (Tables II and III), the rate of production of hydrosulphite continues to be high. The sulphur dioxide, apart from providing

the bisulphite, maintains the system at low pH to promote the formation of hydrosulphite as shown by Patel and Rao (1949).

It was noticed that when excess of sulphur dioxide was passed in the catholyte, a brownish red coloration developed in the catholyte. The colour acted as an index of the excess of sulphur dioxide in the catholyte. The formation of this red colour is a matter of controversy. Meyer (1903) obtained yellow to orange red coloration when hydrosulphite was acidified. Meyer believed it to be due to the formation of dithionous acid, $\text{H}_2\text{S}_2\text{O}_4$. Basset and Durrant (1927) attributed this coloration to the isomeric compound, sulphylic acid, $(\text{HO})_2 \cdot \text{S} \cdot \text{SO}_2$, which they suggested as being formed during acidification of hydrosulphite.

For efficient production of hydrosulphite, sodium bisulphite must always be present in adequate strength in the catholyte. It was noticed that if the concentration of bisulphite was low, the yield of hydrosulphite was adversely affected owing to its reduction to thiosulphate. The optimum concentration range of bisulphite in solution was found to be 20 to 30%.

The production of sodium hydrosulphite can be explained on the basis of the following reactions:—



The last reaction accounts for the maintenance of practically a constant strength of sodium bisulphite in the catholyte (Table VI). This process will, therefore, give us a method of preparing sodium hydrosulphite starting from sodium chloride and sulphur dioxide as the raw materials.

The composition of the anolyte is important from the standpoint of yields of both hydrosulphite and chlorine (cf. Tables IV to VI). If bisulphite is present in the anolyte, it gets oxidised to bisulphate. This not only leads to loss of chlorine but makes the anolyte highly acidic. The hydrogen ions in the anolyte would then move towards the cathode resulting in secondary reactions in the catholyte. The adverse effect of the presence of bisulphite in the anolyte can be seen from the fact that the overall current efficiency for hydrosulphite production drops to 79.7% (Table IV); while in absence of bisulphite in the anolyte, the current efficiency is 90.6% (Table VI). It is, therefore, advantageous to employ only sodium chloride in the anolyte.

Data presented in this investigation show that the temperature of the electrolyte has also a profound effect on the yield of hydrosulphite. When the temperature of electrolysis was 21°C., an average current efficiency of 77.5% was obtained during the first hour of electrolysis (Table X). This went down to 67.2% at the end of the sixth hour. When electrolysis was carried out at 5°C., however, the average current efficiency was 90.6% (Table VI). The lower yield of hydrosulphite at elevated temperatures is principally due to the decomposition of the hydrosulphite into bisulphite and thiosulphate.

The optimum current density for production of hydrosulphite seems to be in the region of 2.0 to 3.0 amp./dm.² The loss in current efficiency at higher current densities seems to be partly due to reduction of hydrosulphite to thiosulphate (Patel and Rao, 1949) and partly to the evolution of hydrogen at the cathode.

In conclusion, it can be stated that the present work has indicated definitely that it is possible to obtain solid hydrosulphite by purely electrochemical method without employing any zinc for the reduction of the bisulphite. By carefully controlling the various factors like temperature, current density, composition of electrolyte, etc., it is possible to keep down the formation of thiosulphate.

SUMMARY.*

The electrochemical preparation of sodium hydrosulphite using a mercury cathode has been studied under various experimental conditions. As a result of this investigation, it has been found practicable to prepare solid hydrosulphite by a purely electrochemical method. Sodium chloride and sulphur dioxide are the principal raw materials employed. Chlorine is obtained as a by-product at the anode. Under optimum conditions, the current efficiencies for the production of sodium hydrosulphite and chlorine were found to be 90.6% and 91.4% respectively.

For efficient production of hydrosulphite by the direct electrochemical method, it is desirable:

- (1) to use mercury as a cathode,
- (2) to employ the catholyte containing 20 to 30% sodium bisulphite together with a high concentration of sodium chloride,
- (3) to employ sodium chloride in its saturated aqueous solution as an anolyte,
- (4) to pass sulphur dioxide to help the formation of bisulphite and consequently to maintain low pH in the catholyte,
- (5) to maintain as low a temperature as possible (5°C.) during the electrolysis,
- (6) to employ a current density between 2 and 3 amp./dm.², at the cathode, and
- (7) to periodically remove the crystals of hydrosulphite from the catholyte.

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* The process for the electrochemical manufacture of hydrosulphite, developed as a result of the investigations described in this publication, has been granted an Indian Patent No. 42313, dated 29th November, 1949.