

STUDIES ON THE ELECTROCHEMICAL PREPARATION OF SODIUM HYDROSULPHITE.

PART V. INVESTIGATIONS ON THE PREPARATION OF HYDROSULPHITE USING METALLIC CATHODES OTHER THAN MERCURY

by C. C. PATEL and M. R. A. RAO, *Department of General Chemistry, Indian Institute of Science, Bangalore.*

(Communicated by Dr. J. C. Ghosh, F.N.I.)

(Received July 7; read October 4, 1952.)

In the previous communication (Part IV), the authors have shown that solid sodium hydrosulphite could be prepared by electrolytic reduction at the mercury cathode, employing sodium chloride and sulphur dioxide as the primary raw materials. Since mercury is an expensive liquid, the suitability of other metallic electrodes is investigated in this paper. K. Jellinek and E. Jellinek (1919) employed platinum, nickel, copper and lead as cathodes and noticed that in the case of lead, hydrosulphite yield was maximum (6.8%), while with other electrodes, the yield was only 3 to 4%. McGlynn and Brown (1929) employed a variety of metallic and amalgamated metallic cathodes and the highest yields (5.5%) were obtained with mercury and amalgamated zinc cathodes. Since the optimum conditions for the preparation of solid hydrosulphite, employing mercury as the cathode, had been fully studied, the suitability of metallic cathodes were also tried under similar conditions.

EXPERIMENTAL.

The electrolytic cell, employed in this investigation, was essentially the same as described in Part IV. The mercury cathode was replaced by a metallic sheet electrode. The materials employed and the methods of analysis were the same as described previously. The experimental conditions employed were as follows: The anolyte was a saturated solution of sodium chloride containing a suspension of the salt. The anode was a graphite rod. The temperature of reduction was 5°C., and the current density at the cathode was 2.05 amp./dm.² The catholyte consisted of 120 ml. of aqueous solution containing about 28% sodium bisulphite and 20% of sodium chloride. Addition of suspension of sodium chloride was avoided in order to find out whether crystals of sodium hydrosulphite were formed during the electrochemical reduction. In this investigation, the cathodes that were employed were (1) zinc, (2) lead, (3) nickel, and (4) iron.

Zinc cathode.—It was noticed during the electrochemical reduction at zinc cathode that no solid got produced in the catholyte for the first one and a half hours, subsequently a greyish white suspension was obtained which on analysis was found to contain zinc hydrosulphite. The cathode was slightly corroded. The details of the results are given in Table I.

It would be noticed from the results of Table I that during the first hour of electrolysis, the current efficiency is greater than 100%. This anomaly is due to the fact that the zinc metal reduces the bisulphite (chemically) to produce hydrosulphite. The current efficiency falls off too rapidly with the progress of time. Added to this, some thiosulphate is also produced during the reduction. The

TABLE I.

Electrochemical preparation of sodium hydrosulphite employing zinc sheet as cathode.

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	3.118	..	22.4	18.4	..	3.74	0.98	151.7	97.3
2	0.35	3.173	..	22.4	17.3	3.63	4.32	1.61	87.6	79.8
3	1.72	3.312	..	23.3	16.9	4.01	4.71	2.23	63.7	73.9
4	1.72	3.284	0.167	23.2	16.3	4.45	5.09	3.00	51.6	74.5
5	1.38	3.562	0.759	23.5	14.8	5.00	5.49	3.80	44.5	75.4
6	1.38	3.562	1.518	23.9	14.1	5.29	5.79	4.54	39.1	75.2

concentration of bisulphite in the catholyte remains fairly steady while that of sodium chloride goes down from 19.8% to 14.1%.

Lead cathode.—During this experiment, it was noticed that hydrogen was evolved at the cathode surface and no crystallisation of the sodium hydrosulphite took place. The catholyte acquired a slight turbidity due to the presence of lead chloride. The results obtained are given in Table II.

TABLE II.

Electrochemical preparation of sodium hydrosulphite employing lead sheet as cathode.

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	1.114	..	25.4	18.1	..	1.34	0.80	54.2	79.9
2	1.04	1.837	0.243	24.7	17.4	..	2.15	1.61	43.5	80.1
3	0.69	2.365	0.433	23.7	16.6	2.365	2.72	2.39	36.7	79.1
4	0.35	2.477	0.623	21.0	16.5	2.657	3.02	3.12	30.6	77.5
5	1.04	2.505	1.139	19.5	16.3	2.832	3.18	3.87	25.8	76.8
6	0.35	2.365	2.171	17.3	16.2	2.853	3.18	4.46	21.5	73.8

The results given in Table II indicate that the maximum concentration of hydrosulphite is only 2.85% with a current efficiency of 21.5% at the end of six hours. The thiosulphate production is higher than that at zinc cathode. The bisulphite content diminishes gradually with the progress of electrolysis while concentration of sodium chloride remains more or less constant. The fall in the concentration of bisulphite is due to the reduction in the consumption of sulphur dioxide.

Nickel cathode.—During the electrolysis using nickel cathode, the catholyte acquired a slightly brown colour. No crystals of sodium hydrosulphite were formed. Some hydrogen was evolved at the cathode. There was no detectable corrosion of the cathode. The results obtained are given in Table III.

The results of Table III indicate that there is a rapid decrease in current efficiency for hydrosulphite formation. The current efficiency for chlorine remains at about 77%. There is increasing formation of thiosulphate with the progress of electrolysis.

TABLE III.

Electrochemical preparation of sodium hydrosulphite employing nickel sheet as cathode.

Time in hours	SO ₂ passed g./hr	Composition of filtered catholyte, g. in 100 ml. soln.				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	1.336	..	26.6	18.6	1.60	0.85	65.0	84.7
2	0.35	1.754	0.213	25.3	17.2	2.16	1.54	43.8	76.2
3	1.73	2.115	0.547	25.4	16.9	2.58	2.31	34.8	76.4
4	1.04	2.199	1.139	23.8	16.4	2.67	3.14	27.1	77.8
5	0.35	2.282	1.457	21.6	16.1	2.76	3.91	22.4	77.7
6	0.35	2.255	2.505	17.9	15.8	2.74	4.65	18.5	76.9

Iron cathode.—Evolution of hydrogen was noticed at the iron cathode during the electrolysis. The catholyte developed a white turbidity but the filtrate was colourless. The surface of the cathode was found to have blackened at the end of the experiment. The results obtained in this experiment are given in Table IV.

TABLE IV.

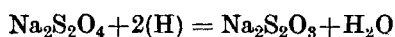
Electrochemical preparation of sodium hydrosulphite employing iron sheet as cathode.

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	1.336	..	27.1	18.1	..	1.60	0.81	65.0	80.7
2	1.04	1.614	0.35	26.7	17.4	..	1.84	1.66	37.3	82.5
3	0.69	1.670	0.88	25.8	16.6	1.936	2.25	2.40	30.4	79.6
4	0.35	1.726	2.11	22.9	16.5	1.941	2.26	3.20	22.9	79.3
5	1.04	1.848	2.50	22.8	16.3	2.005	2.31	3.90	18.7	77.5
6	0.35	1.892	3.34	22.7	16.2	2.019	2.32	4.47	15.6	74.0

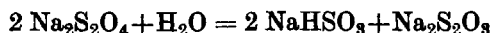
The results represented in Table IV indicate that the current efficiency at the end of the experiment is very low (15.6%) for the production of hydrosulphite. The current efficiency for the production of chlorine varied from 82.5% to 74.0%. Thiosulphate formation was maximum with this cathode.

DISCUSSION.

A scrutiny of the data presented in this paper shows that in presence of metallic cathodes, production of hydrosulphite is low when compared with the experiments with the mercury cathode. The low yield may be attributed to the following: (1) evolution of hydrogen at the cathode, causing dissipation of electrical energy and (2) formation of thiosulphate in the catholyte by reduction of hydrosulphite. The formation of thiosulphate during the preparation of hydrosulphite has been attributed by Elbs and Becker (1904) to the electrolytic reduction of hydrosulphite at the cathode in terms of the reaction:



On the other hand, K. Jellinek (1911) states that the thiosulphite is formed by spontaneous decomposition of hydrosulphite as per equation:



During the course of the preparation of hydrosulphite, employing mercury as the cathode, very little of thiosulphate was produced in the catholyte (Part IV). With the other metal electrodes, however, considerable quantities of thiosulphate were produced. The formation of thiosulphate, therefore, seems to be due to the electrolytic reduction of hydrosulphite rather than to the spontaneous decomposition of the latter.

There is apparently a close correlation between the efficiency of the cathode and its hydrogen over-voltage as shown in Table V.

TABLE V.

Effect of hydrogen over-voltage on the production of hydrosulphite.

Electrode used	Hydrogen over-voltage by		At the end of electrolysis of six hours			
	Newbery (1916).	Caspari (1899).	$\text{Na}_2\text{S}_2\text{O}_4$ in 100 ml. of catholyte. g.	$\text{Na}_2\text{S}_2\text{O}_3$ in 100 ml. of catholyte. g.	Overall current efficiency for $\text{Na}_2\text{S}_2\text{O}_4$. %	
Iron	0.18	0.08 (in NaOH soln.)	2.02	3.34	15.64	
Nickel	0.18	0.21	2.26	2.51	18.49	
Lead	0.46	0.64	2.85	2.17	21.51	
Zinc	0.72	0.70	5.29	1.52	39.11	
Mercury	0.70	0.78	12.53	Nil	85.70	

As the hydrogen over-voltage at the cathode rises, conditions for the formation of hydrosulphite are far more favourable. It is known that hydrogen is discharged much more readily than sodium at cathodes having low hydrogen over-voltage (Mantell, 1940). In the case of the mercury cathode, owing to its high hydrogen over-voltage, conditions are less favourable for the evolution of hydrogen and consequently the liberation of sodium is favoured. The sodium thus produced brings about the reduction of bisulphite to hydrosulphite.

It will be noticed that though zinc and mercury have hydrogen over-voltage of the same order, production of hydrosulphite is much greater at the mercury cathode. This seems to be due to the fact that the sodium liberated at the mercury cathode, readily forms an amalgam. Formation of amalgam leads to conservation of sodium (by reducing its reactivity with water) and makes it more available for the formation of hydrosulphite. A good part of the sodium liberated on the zinc cathode, on the other hand, is lost by its reaction with water. This explains the low current efficiency at the zinc electrode.

SUMMARY.

Electrochemical preparation of sodium hydrosulphite has been carried out using non-mercury cathodes like iron, lead, nickel and zinc, and the results have been compared with those

at a mercury cathode. An explanation is offered for the possible correlation noticed between hydrogen over-voltage of the cathode and its efficiency in the electrochemical reduction of bisulphite to hydrosulphite.

The authors are thankful to Sir J. C. Ghosh and Dr. B. Sanjiva Rao for their keen interest in the work.

REFERENCES.

- Caspari, (1899). Ueber elektrolytische Gasentwicklung. *Z. physik. Chem.*, **30**, 89.
Elbs and Becker, (1904). Versuche zur elektrochemischen Darstellung unterschwefligsaurer (hydroschwefligsaurer) Salze. *Z. Elektrochem.*, **10**, 361.
Jellinek, (1911). Ueber die elektrolytische Herstellung von Hydrosulfit aus Bisulfitlösung. *Z. Elektrochem.*, **17**, 245.
Jellinek and Jellinek, (1919). Chemische Zersetzung und elektrolytische Bildung von Natriumhydrosulfit. *Z. physik. Chem.*, **93**, 325.
McGlynn and Brown, (1929). Preparation and evaluation of hydrosulphites. *J. Phys. Chem.*, **33** (ii), 1665.
Mantell, (1940). Anodic and cathodic processes. *Industrial Electrochemistry*. (McGraw-Hill Book Co., Inc., New York and London, 2nd Edition), p. 335.
Newbery, (1916). Overvoltage tables, Part III. Overvoltage and the periodic law. *J. Chem. Soc.*, **109**, 1107.

Issued April 21, 1953.