

ELECTROLYTIC PREPARATION OF SODIUM PERBORATE

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The preparation of sodium perborate has been investigated by electrolysing a solution of borax and sodium carbonate with a platinum anode and stainless steel cathode. The effect of concentrations of borax and sodium carbonate, temperature and anode current density on current efficiency of perborate formation was studied.

Key words: Electro-oxidation, sodium perborate, platinum anode

INTRODUCTION

Among the persalts, sodium perborate finds extensive use as a component in bleaching and in dentrifices. Chemical method of preparation of sodium perborate is done by reacting hydrogen peroxide with sodium tetraborate [1]. Literature shows that there are a number of references for the preparation of sodium perborate by electrolytic method [2]. However, there are wide variations in the operating conditions in the processes referred. It was, therefore, considered necessary to study carefully the optimum conditions for the electrolytic preparation of sodium perborate on a laboratory scale, as preliminary to the setting up of large-sized cells. No plant for the manufacture of sodium perborate by electrolysis exists in the country at present.

The present paper deals with the preparation of sodium perborate by electrolysing a solution of borax and sodium carbonate with a platinum anode and stainless steel cathodes. The effect of concentrations of borax and sodium carbonate, temperature and anode current density on current efficiency of formation of sodium perborate has been studied and the results are presented in this paper.

EXPERIMENTAL

Cell assembly

The cell assembly consisted of a pyrex dish of about 900 ml capacity acting as cell with a cell cover made of PVC with suitable slots and holes to introduce electrodes, thermometer and cooling coil. A platinum foil (50 x 50 x 0.075mm) was used as the anode. The top portion of the platinum foil was gripped and sandwiched between two copper strips (0.3mm thick) and tightened by means of bolts inserted above the platinum sheets and electrical connection was given to the copper portion. The cathodes were made of stainless steel plates (5cm x 5cm x 1.5mm) wrapped with white asbestos rope and fixed on either side of the anode. Anode-cathode spacing was 1 cm. A glass cooling coil was immersed into the electrolyte through which cooled methanol was circulated to maintain the temperature of the electrolyte at the desired values. In earlier experiments, the cooling was done by using ice and salt (freezing mixture) in an outer vessel. 850 ml of electrolyte containing borax (30-50 g/l), sodium carbonate (100-150 g/l), sodium bicarbonate (25 g/l) and magnesium silicate (1 g/l) was taken in the cell and after the temperature had attained the desired value, the electrolysis was started with the help of a rectifier (0-12V, 25A). In all the

TABLE-I: Variation of concentration of borax on current efficiency. $\text{Na}_2\text{CO}_3 = 130 \text{ g/l}$; $\text{NaHCO}_3 = 25 \text{ g/l}$; $\text{MgSiO}_3 = 1 \text{ g/l}$; Current = 6A; Anode C.D. = 2KA, m^{-2} ; Temp. = 288K; Quantity of electricity = 12 A hrs; current concentration = 7a/l. Volume of electrolyte = 850 ml

S.No.	Concentration of borax (g/l)	Voltage (V)	Concn. of perborate formed (g/l)	Current efficiency (%)	Energy consump- tion (Kwh/kg)
1(a)	30	4.52	4.3	20.0	7.9
(b)*	28	5.40	5.3	26.2	7.2
2(a)	40	4.66	6.7	29.9	5.4
(b)*	40	5.70	8.4	41.0	4.9
3	50	4.58	4.2	19.4	8.2

* Cooling by freezing mixture taken in an outer vessel

TABLE-II: Variation of concentration of Na_2CO_3 on current efficiency: Borax = 40 g/l; (other conditions same as in Table I)

S.No.	Concentration of Na_2CO_3 (g/l)	Voltage (V)	Concn. of perborate formed (g/l)	Current efficiency (%)	Energy consumption (kwh/kg)
1	100	4.9	4.9	22.9	7.5
2(a)	130	4.7	6.7	29.9	5.4
(b)*	130	5.7	8.4	41.0	4.9
3	150	4.68	6.5	30.3	5.4

* Cooling by freezing mixture taken in an outer vessel

TABLE-III: Variation of temperature on current efficiency. Borax = 40g/l (other conditions same as in Table I)

S.No.	Temperature (K)	Voltage (V)	Concn. of perborate formed (g/l)	Current efficiency (%)	Energy consumption (kwh/kg)
1	278	4.93	6.8	31.8	5.4
2	283	4.85	6.0	28.0	6.0
3(a)	288	4.70	4.2	29.9	5.4
(b)*	288	5.70	8.4	41.0	4.9
4*	298	5.00	5.5	27.2	6.4

* Cooling by freezing mixture taken in an outer vessel

TABLE-IV: Variation of anode current density on efficiency: Temperature = 278K (other conditions same as in Table III)

S.No.	Current (A)	Anode current density (ka.m^{-2})	Voltage (V)	Concn. of perborate formed (g/l)	Current efficiency (%)	Energy consumption (kwh/kg)
1	3*	1	3.85	4.2	8.8	15.3
2	6	2	4.93	6.8	31.8	5.4
3	6	3	5.4	6.5	30.1	6.2

(* Volume of electrolyte = 380ml and using a different set up)

experiments the same quantity of electricity (12 A hrs) was passed. The current efficiency was calculated after analysing the final solution with permanganate [3].

RESULTS AND DISCUSSION

Tables I and IV show the results of experiments carried out for the preparation of the sodium perborate.

Effect of concentration of borax

The effect of concentration of borax on current efficiency was studied and the results are presented in Table I. It is seen that the concentration of the borax at 40 g/l gives the maximum current efficiency. When freezing mixture is used to maintain the temperature, the current efficiency is much better. Earlier reported results, though indicate the concentration of borax from 16 to 40 g/l [4-7], do not give the effect of variation of concentration of borax on current efficiency. Some authors recommend using excess borax so that the solution is continually saturated with this compound during electrolysis.

Effect of concentration of sodium carbonate

It is seen from Table II that a concentration of 130-150 g/l sodium carbonate behaves better. By maintaining the temperature with freezing mixture, a better current efficiency is obtained. This concentration range confirms the reported values [4-8]. It has also been reported [9,10,23] that increase of carbonate concentration increases current efficiency. Further, it is reported [10] that sodium or potassium hydroxide, instead of sodium carbonate, yields no perborate.

Effect of addition agent

A number of addition agents have been reported [4-8, 10-18], like turkey red oil, magnesium silicate etc. for improving the current efficiency in the preparation of perborates and among them magnesium silicate has been claimed to be the best, which is prepared by the reaction of magnesium sulphate with sodium silicate [19]. Magnesium ion itself reduces the decomposition of perborate [20] while silicate also acts as a good stabiliser. Other cations viz. Cu^{++} , Fe^{+++} , Pb^{++} and Hg^{++} , however, increase the speed of decomposition.

Accordingly when experiments were carried out with the addition of magnesium silicate, the current efficiency increased from 29.6% to 41% with the addition of the additive. However, with the addition of sodium silicate alone the current efficiency was 35.9%. Hence magnesium silicate (1 g/l) was used in all the experiments. But the effect of various addition agent and their concentrations on the current efficiency is yet to be studied in detail. Other addition agent which is reported to be effective is boric acid. Recent literature shows [5,8,16,18,21,22] the use of addition agents like urea, phosphate, thiocyanate, sodium rhodanide, disodium-EDTA, sodium or magnesium nitrates, sodium chloride and ammonium sulphate for improving the voltage and yield and for reducing platinum consumption.

Effect of temperature on current efficiency

There is no marked variation in current efficiency with temperature

from 278 to 288K (Table III). It is well known that higher temperature favours the decomposition of perborate. It also increases the rate of discharge of water as against the discharge of carbonate ions, the latter being one of the steps in the formation of perborate.

Effect of anode current density on current efficiency

The current efficiency increases with anode current density from 1 to 2KA. m^{-2} and remains almost constant at higher current density viz. 3KA. m^{-2} . The reported values vary from 0.8 to 8KA. m^{-2} . The present results also confirm the earlier observations that current efficiency increases with current density [10,23]. Contrary to this, it is also reported that increase of current density decreases the current efficiency [24] due to increased loss of active oxygen at the higher current density [25].

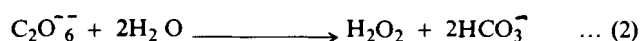
CONCLUSION

The mechanism by which perborate forms by electrolysis has the following steps [26]:

(i) Electrolysis step.



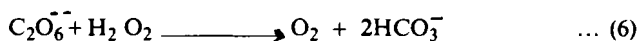
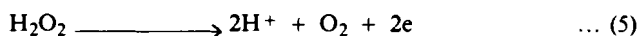
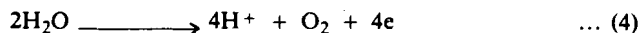
(ii) Hydrolysis step



(iii) Oxidation step



But there will be a number of other side reactions which may contribute to the decrease in the efficiency, viz.



In addition, chemical disproportionation reaction of H_2O_2 can also take place. Thus one can see that the current efficiency is dependent on a complex interplay between these various reactions [21], which again can be influenced by the operating parameters like potential, concentration of electrolyte, temperature etc.

REFERENCES

1. A Regner, *Electrochemical processes in chemical industries*, Constable & Co.Ltd. (London) (1957) p 424
2. Z Nagy, *Electrochemical synthesis of inorganic compounds - A bibliography*, Plenum Press, N.Y. (1985) p 26,296.
3. (Ed) A.N. Furmann, *Scot's standard methods of chemical analysis*, V Edition, Van Nostrand, Princeton N.J., (1939) p 2036
4. S S Markov, G A Seryshev, V I Gribel, N I Nekrasova, T N Cherkazova and G D Ivanova, USSR 581,170 (1977); C.A.88 (1978) 96701

5. A M Alekhin, Yu A Khokhlov, A N Lazarev, V M Arkhipova, V P Berdyushina and A S Shubin, U.S.S.R. 1,109,480 (1984) CA 101,179982 (1984)

N T Toroptseva, N E Khomutov and T A Niftullaeva, Deposited Dec.1981, VINITI 1503-81, 10pp(Russ) CA 97 (1982) 46505
7. Y Yamaguchi and E Shindo, *J Electrochem Assoc (Japan)*, 2 (1934) 126
8. S N Ershov, V M Arkhipova, V P Berdyugina, P G Permyakov, V I Zavatskii, Yu A Khokhlov, N B Kondrikov and T P Fedorova. USSR 941,431 (1982) C.A 97 (1982) 153132.
- 9 D S Kim, J M Kim and W M Kim, *Guklip Kongop Yonguso Yongu Pogo*, 22 (1972) 35; C.A. 83 (1975) 34759
10. J R Matsuda, *Bull chem Soc (Japan)*, 11 (1936) 456
11. F Kawamura, *J Elettrochem Assoc (Japan)*, 1 (1933) 262
12. F Kawamura and H Mohri, *ibid* 2 (1934) 10
13. N N Drozin, *Zhr Priklad Khim*, 24 (1951) 86
14. P Mollard, USP 3,038,842(1962) C.A. 57 (1962) 12257
15. S S Markov, G A Seryshev, V V Stryuk, N I Nekrasova and E A Brusnickina U.S.S.R. 323442 (1975) C.A.83 (1975) 105466
16. G A Seryshev, V I Gribel, N I Nekrasova, N A Gemzaeva, *Zhur Priklad Khim*, 51 (1978) 827; CA 89(1978) 50517g
17. G A Seryshev, N I Nekrasova, V I Gribel, G D Ivanova, T N Klyueva and N A Gamzaeva, *ibid*, 52 (1979) 1752; CA 91 (1979) 165542
18. A M Alekin, V M Arkhipova, V P Berdyugina, P G Permyakov, V I Zovatskii, A N Lazarev and N V Zavertyaeva U.S.S.R. 1,096,308 (1984) CA101 (1984) 139822
19. A Ya Futoryanskii, E K Kaverzin, K V Tkachev, V G Shkradov, V M Simrnov and G G-Dreganov, U.S.S.R. 998,340, (1983) C.A.99 (1983) 24940
20. S Kuhnel Hagen and V Ahrend Larsen, *Angew Chem*, 45 (1932) 290
21. S N Ershov, V M Arkhipova, Yu A Khokhlov, G Ya Eremenko, V I Zavatskii, and A N Lazarev, U.S.S.R. 920,080, (1982) C.A. 97 (1982), p63115q
22. S N Ershov, V M Arkhipova, V P Berduygina, P G Permyakov, V I Zavatskii, Yu A Khokhlov, N B Kondrikov and T P Fedorova, U.S.S.R. 941,431. (1982) CA 97 (1982) 153132x
23. P M V D Wiel, L J J Janssen and J G Hoogland, *Electrochim, Acta*, 16 (1971) 1221,1227.
24. N T Toroptseva, T A Niftullaeva, N E Khomutov, G D Gonchar and Yu A Khokhlov, *Deposited Dec*, 1981. VINITI 2809-81, 15pp(Russ) C.A. 97 (1982) 81629q
25. F Giordani and R Intonti *Rend Acad Sci (Napoli)*, 34 (1928) 30 C.A.23 (1929) 2371.
26. B Mario. Italian 634281 (1962)