Technical Paper

Preparation of Tetramethyl Ammonium Hydroxide by Electrolysis

S. KRISHNAN*, G. S. SUBRAMANIAN** and H.V.K. UDUPA**

(* Deputy Chief Chemist, Indian Telephone Industries,
Bangalore, India
** Central Electrochemical Research Institute, Karaikudi, S. India)

(Received July 25, 1970)

The paper deals with the preparation of pure tetramethyl ammonium hydroxide solution by electrolysis of tetramethyl ammonium chloride using ion exchange membrane. By this technique in a three compartment cell, it is possible to obtain the desired concentration of tetramethyl ammonium hydroxide in the central compartment continuously. The solution obtained is free from chloride and is suitable for use as electrolyte in the cathodic dimerisation of acrylonitrile to adiponitrile. The details of the cell and the conditions of electrolysis are described in the paper. The average current efficiency is 50% in most of the electrolysis.

1 Introduction

Tetramethyl ammonium salts and their solutions are good supporting electrolyte and are largely employed in polarographic studies. Recently tetramethyl ammonium hydroxide solution has been successfully used as electrolyte for the cathodic dimerisation of acrylonitrile to adiponitrile¹. The tetramethyl ammonium hydroxide for this purpose must be free from chloride ions or metal ions as their presence in the solution hinders the efficiency of dimerisation and lead to the formation of larger amounts of propionitrile². It becomes therefore necessary to work out a suitable method of preparing tetramethyl ammonium hydroxide in a pure state.

Walker and Johnson³ have described a method for preparing the hydroxide by interaction of potassium hydroxide and tetramethyl ammonium chloride in alcoholic solution and have shown how definite hydrates of the quarternary base may be separated from the solution obtained. Thus a tetra hydrate of the hydroxide has been prepared by the above method⁴. These chemical methods have the disadvantage in that the hydroxide so prepared are not suitable for cathodic dimerisation studies on account of the presence of chloride and potassium ions present in them.

The electrolysis of aqueous solutions of tetramethyl ammonium chloride solutions using a mercury cathode in the normal chlor-alkali cells will not be suitable

also since the product is very difficult to be purified free from the chloride. Further, it is reported that such a process may lead to reductive fission of the product⁵.

Krokh⁶ has suggested a three compartment cell using ion exchange membranes for the preparation of pure tetramethyl ammonium hydroxide solution. Instead of tetramethyl ammonium chloride as used by Krokh⁶, electrolysis of tetramethyl ammonium iodide solution between graphite and iron cathodes in the electrodialysis cell separated into three compartments by cation exchange membrane and by a ceramic diaphragm at a current density of 3 A/dm² has been described⁷. The use of cellophane membranes instead of ion exchange membranes has been suggested⁸. The effect of additions in the anodic compartment has been investigated with the objective of stabilising the optimum conditions for the electrolysis⁹.

The survey of the available information so far has revealed that not much work has been done to work out a suitable method for the preparation of tetramethyl ammonium hydroxide by electrolysis and such a study was found to be necessary in connection with our investigation on the cathodic dimerisation of acrylonitrile. The results of our investigation on the preparation of tetramethyl ammonium hydroxide in a pure state by electrolysis are presented in this paper.

Table 1
Conditions: As mentioned above

Cell voltage (volts)	Amp-hrs passed	Total volume of solution	Total wt. of TMAH in solution (g)	Increase in wt. of TMAH in solution (g)	Concentration (%)	Current efficiency (%)
10.5	1.35	315	25.13	3.10	8.0	67.5
9.5	3.00	325	31.13	6.00	9.6	58.9
8.5	7.67	350	45.81	14.68	13.1	56.3
8.0	11.00	366	64.17	18.36	17.5	49.0
6.5	12.00	380	87.64	23.47	23.1	54.2
6.0	13.00	400	107.84	20.20	27.0	48.6
6.0	15.00	423	132.84	25.00	31.4	49.3

2 Experimental

The cell is made from Perspex and has three compartments. It is provided with A-20 anion exchange membrane and C-20 cation exchange membrane as diaphragms mounted on Perspex frame. The capacity of the middle compartment is 300 ml while extreme compartments are 250 ml each. The anion and cation exchange membranes are chemically and electrochemically converted to OH and tetramethyl ammonium forms respectively. A perforated iron plate with an effective area of 0.3 sq. dm is used as cathode while a graphite plate with an effective area of 0.2 sq. dm is used as anode. A current density of 7 A/dm² is used. Catholyte is 9% sodium hydroxide and anolyte is 90% tetramethyl ammonium chloride solution. The central compartment is filled with pure water. The initial voltage of the cell is high but as the electrolysis proceeds the conductivity increases due to formation of the tetramethyl ammonium hydroxide in the central compartment. The current efficiency is determined by estimating the strength of the tetramethyl ammonium hydroxide in the central compartment. As the electrolysis proceeds, the level in the central compartment increases and it can be continuously syphoned out. The rate of feed at the extreme compartments can be adjusted, depending on the concentration of the hydroxide solution desired from the central compartment and the technique can thus be made to produce continuously the desired concentration of the tetramethyl ammonium hydroxide solution in a pure state. The material so obtained is free from chloride ion as well as metallic impurity and is highly suitable for the dimerisation studies.

3 Results and Discussion

Table 1 gives the results obtained with such a cell. From the Table, it is clear that it is possible to build up any concentration and the average current efficiency is nearly 50%. The formation of tetramethyl ammonium hydroxide in the central compartment is the result of migration of tetramethyl ammonium ion from the anode chamber having the cation exchange membrane and OH ion from the cathode chamber containing the anion exchange membrane. It is interesting to note that the average current efficiency for any desired concentration range is 50% and the balance of the current is used for the transport of other ionic species.

As mentioned earlier, the process can be made continuous. The solution is free from chloride or metallic ions. The solution can be concentrated under reduced pressure to get the solid tetramethyl ammonium hydroxide.

Acknowledgment: The authors thank Professor K. S. G. Doss, former Director of the Institute for his keen interest in the problem.

References:

- 1) F. Deck, *Chem. Ing. Tech.* **37** (No. 6), 607 (1965).
- 2) M. Baizer, *J. Electrochem. Soc.*, 216 (1964).
- 3) Walker, Johnson, *J. Chem. Soc.* **87**, 955 (1905).
- 4) D.C. Crichton, *J. Chem. Soc.* **91**, 1794 (1907).
- 5) L. Horner, A. Mentrup, *C.A.* **61**, 12952 (1964).
- 6) V.V. Krokhr, *J. Appl. Chem. USSR* **37** (No. 10), 2293 (1964).
- 7) N. A. Ozbanovski, V. V. Tsodikov, L. D. Borkhi, R. T. Khleborodova, *C.A.* **61**, 3925 (1964).
- 8) G.S. Supin, *J. Phy. Chem. USSR* **34**, 925 (1960).
- 9) G.S. Supin, *C.A.* **55**, 6214 (1961).