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SHORT COMMUNICATION

Electrosynthesis of quaternary ammonium hydroxides

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1. Introduction

Quaternary ammonium hydroxides (QAH) are very useful phase transfer catalysts [1–3] as well as intermediates for synthesizing quaternary ammonium salts (QAS) by neutralization with the appropriate acid. QAS have found great use in phase transfer catalysis and as supporting electrolytes in electroorganic synthesis [4] and electroanalyses.

From an industrial point of view, QAH and QAS are not easily available and their cost is high. Thus, it is necessary to develop processes to synthesize these compounds starting from relatively cheap and easily available raw materials such as quaternary ammonium chlorides and bromides.

Three major methods have been reported in the literature for the preparation of QAH: (a) reaction of quaternary ammonium chloride or bromide with silver oxide. This method is limited by the use of relatively expensive reagents; (b) anion exchange between potassium hydroxide and quaternary ammonium chloride or bromide in alcoholic solution. This method is generally limited because the yields are not quantitative and therefore QAH becomes contaminated with both starting materials and by product potassium halide, which does not precipitate completely; and (c) electrolysis using a divided cell in which the anolyte is an aqueous solution of quaternary ammonium chloride and is separated from the catholyte by means of a cation exchange membrane [5, 6]. As a result, a pure aqueous solution of QAH is obtained in the catholyte. The method works well with quaternary ammonium cations of low molecular weight such as tetramethylammonium. However, as the cation size increases, the migration from anolyte to catholyte across the cation exchange membrane becomes more difficult. Thus, a membrane polarization arises, faradaic yield decreases and power consumption increases in such a way that the process is not suitable for industrial application [7].

In this paper, an efficient process to electrosynthesize QAH in aqueous solution in a divided filter press cell, in which anodic and cathodic compartments are separated by an anion exchange membrane, is reported. The catholyte is an aqueous solution of a quaternary ammonium chloride or bromide. During electrolysis, chloride or bromide anions migrate from catholyte to anolyte and are substituted by the hydroxyl anions electrogenerated in the cathode. As the ion transferred is always the anion of small size, it is possible to obtain QAH of both low and high molecular weights. Therefore, the undesirable problems that appear when using the previously described method (c) are overcome.

If the starting material is not soluble in water, the electrolysis can be carried out in methanol, ethanol or mixtures of these solvents with water. Thus, due to its versatility, high productivities and low power consumption, makes the process very attractive from an industrial point of view.

2. Experimental details

The preparative electrolyses were carried out at constant current using both a Promax FAC-365 (5 A, 30 V) and an OMI rectifier (10 A, 30 V). A parallel-plate, filter press assembly was used as a flow cell with a RuO_2/Ti anode and a stainless steel cathode, both of 20 cm^2 electrode area, separated by an anion exchange membrane. In some experiments the anode was graphite JP845 (Le Carbone-Lorraine). The interelectrode gap was 8 mm. Propylene mesh between the membrane and the electrode prevented contact and at the same time was used as a turbulence promoter. Both electrolytes were contained in two 0.5 dm^3 jacketed glass reservoirs and were pumped through their respective compartments by means of two magnetic pumps (Iwaki MD-20-R) to provide flow rates of 2 l min^{-1}. Temperature controlled recirculating water through the jackets of the reservoirs. The anolyte was either a solution of HCl or HBr in water or alcohol–water mixtures, or a solution of NaCl or NaBr in the same solvent. The catholyte was a solution of quaternary ammonium chloride or bromide in water, alcohol or mixtures of both solvents. Quaternary ammonium chlorides and bromides were supplied by Merck and used without further purification.

The electrolysis was stopped when the quantity of chloride or bromide ions in the catholyte was less than 0.10%. QAH concentration was determined by titration.

3. Results and discussion

QAH can be obtained by this electrochemical method according to the following equations:

cathodic reaction

$$\begin{gathered} 2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \\ 2R_4NX + 2OH^- \longrightarrow 2R_4NOH + 2X^- \end{gathered} \quad (1)$$

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Table 1. Electrosynthesis of quaternary ammonium hydroxides (QAH) in a divided filter press cell

Entry	*Substrate*	*Solvent*	Cs^a	T^b	D^c	$C_{QAH}{}^d$	V^e	Ec^f	S^g	P^h	SEC^i
1	A	H_2O	10	25	2000	8.25	7.8	17	100	3.22	4.8
2	A	H_2O	5	25	2000	4.13	9.5	23.5	100	4.5	4.3
3	A	H_2O	10	25	2700	8.40	9.8	17	100	4.4	6.0
4	A	H_2O	10	45	2700	8.35	7.5	25	100	6.2	3.3
5	B	H_2O	6.5	32	2700	4.5	6.9	18.5	100	2.8	6.6
6	C	H_2O	10	35	2700	9.0	8	19.5	100	4.1	5.3
7	A^j	$MeOH/H_2O$ (95%)(5%)	15	30	2700	13.0	20	28	100	7.6	7.0
8	D^j	$MeOH/H_2O$ (99.5%)(0.5%)	7.5	25	2500	6.70	28	7	100	3.0	23

[a] Substrate concentration (% w/w), [b] temperature (° C), [c] current density ($A\,m^{-2}$), [d] final quaternary ammonium hydroxide concentration (% w/w), [e] mean cell voltage (V), [f] faradaic yield (%), [g] chemical yield (%), [h] productivity ($kg\,QAH\,h^{-1}\,m^{-2}$), [i] specific energy consumption ($kWh\,kg^{-1}$), and [j] anode graphite JP-845. Anolyte 7.7% NaBr in MeOH.

Separator anion exchange membrane: Selemion AMV (entries 1–3, 5); Neosepta ACLE-5P (entry 4); Neosepta AFN (entries 6, 7); Tosflex IE SA 48 (entry 8). Electrode area $20\,cm^2$. Anode RuO_2/Ti.

Cathode Stainless Steel 316. A = tetrabutylammonium bromide. B = tetraethylammonium bromide. C = benzyltriethylammonium chloride. D = tetra *n*-octylammonium bromide. In all cases the final halide concentration in the catholyte was less than 0.1% w/w.

anodic reaction

$$2X^- \longrightarrow X_2 + 2e^- \tag{2}$$

overall reaction

$$2R_4NX + 2H_2O \longrightarrow 2R_4NOH + X_2 + H_2 \tag{3}$$

The halide ion migrates across the anion exchange membrane from the catholyte to the anolyte where it is oxidized to the halogen. In the cathode, hydroxyl ions are produced and they substitute the halide ions in such a way that if sufficient charge is passed, at the end of the electrolyses a pure solution of QAH is obtained in the catholyte.

In Table 1 electrolysis conditions and results for four QAH are given. As can be seen faradaic yields are low since hydroxyl ions compete with the halide ions in migration through the anion membrane. However, due to the high molecular weight of these chemicals, the high current densities applied and the fact that in the electrochemical reaction $1\,F\,mol^{-1}$ is involved, both high specific productivities ($kg\,h^{-1}\,m^{-2}$) and low specific power consumptions ($kWh\,kg^{-1}$) are very promising from an industrial point of view. Thus, the results are equal or better than those obtained in the electrosynthesis of a QAH of low molecular weight such as tetramethylammonium hydroxide, using the method (c) described in the introduction [6] ($3.5\,kg\,h^{-1}\,m^{-2}$; $3.14\,kWh\,kg^{-1}$). The feasibility of our method becomes evident when comparing the results obtained in the electrosynthesis of tetra *n*-butylammonium hydroxide in water (entries 1–4 in Table 1) with those obtained by means of method (c), which uses Nafion 324 cation membrane to separate the anodic and cathodic compartments. In this case, a cell voltage higher than 30 V is produced at a current density lower than $100\,A\,m^{-2}$ [7].

Only in the case of entry 8 was the power consumption too high, due to the need to use a very low amount of water in both anolyte and catholyte, since the substrate is insoluble in water. The reaction was not optimized and it is therefore reasonable to assume a dramatic decrease in the power consumption by a careful choice of both the solvent composition and the current density.

In laboratory experiments we have used Neosepta AFN and Neosepta ACLE-5P both from Tokuyama Soda, Selemión AMV from Asahi Glass and Tosflex IE SA 48 from Tosoh Corporation as anion exchange

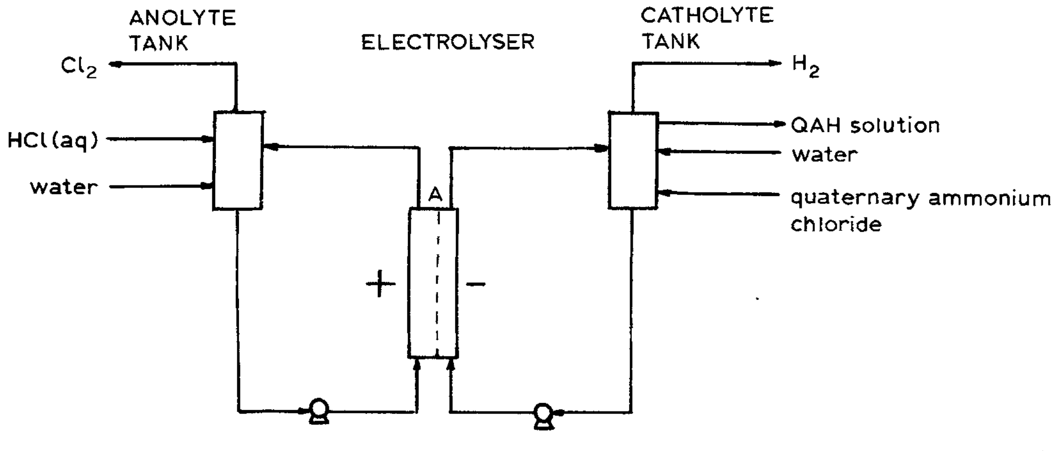

Fig. 1. Flow diagram to produce an aqueous solution of quaternary ammonium hydroxide from quaternary ammonium chloride. A = anion exchange membrane.

membranes. All suffer from poor stability in basic solutions. Consequently the final concentrations of QAH obtained at the end of the electrolyses have to be low. In spite of these low concentrations, the membrane life can be seriously shortened in industrial production.

Thus, the economic penalty is obvious. This limitation can be overcome by using a Tosflex IE SF 34 anion exchange membrane, in which concentrations of QAH as high as 25% w/w can be obtained without affecting their long-term stability. A flow-diagram of the process to produce an aqueous solution of QAH is outlined in Fig. 1.

4. Conclusions

Compared to the methods reported earlier to produce quaternary ammonium hydroxides, the present method is a good, simple and economic alternative to obtain these compounds, mainly for QAH of high molecular weight.

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