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Studies on the synthesis of sodium ates (NaH_2PO_4, Na_2HPO_4, Na_3PO_4) using membrane electrolysis

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Abstract

Comparative studies have been carried out on the electrosynthesis of sodium phosphates in the cathode compartment of an industrial membrane cell supplied with phosphoric acid of concentrations ranging from 1 to 2 mol dm^{-3}. The anode compartment of the cell was supplied with brine containing 25% NaCl. Du Pont Nafion® membranes of types N-423, N-901 and N-961 were used. It was found that current efficiencies for the production of sodium phosphates exceeded 96%, this being higher than that for sodium hydroxide and, in spite of the different properties of the membranes, these efficiencies were similar. With N-423 membrane, the current efficiency was 2 ~ 3% lower than that for other membranes, but at the same time, the voltage of the cell was lower by 8 ~ 12%. Thus, N-423 membrane gives better performance during sodium phosphate synthesis as compared to membranes N-901 and N-961.

1. Introduction

Electrosynthesis of sodium *o*-phosphates (NaH_2PO_4, Na_2HPO_4, Na_3PO_4) using the membrane method, involves supplying phosphoric acid (instead of water) with acid of such concentration and flow rate to obtain the desired composition. Sodium chloride solution in the anode compartment provides Na^+ ions for the reaction. During electrolysis, Na^+ ions penetrate the cation-exchange membrane from the anode to the cathode at a velocity and mass flow rate depending on the membrane and electrolysis parameters (Figure 1).

The aim of this study is to determine the conditions and parameters for obtaining high purity sodium phosphates. Purity grade depends on high purity of the media used in membrane electrolysis. Assuming that the relevant anolyte requirements [1] are met, such purity may be achieved if the cathode compartment is supplied with thermal phosphoric acid solution prepared with distilled water. This acid can be additionally purified, if necessary [2]. However, modification of typical raw material supplied to the phosphoric acid cathode compartment changes the conditions prevailing in this compartment to such an extent that determination of the influence of the changed conditions (i.e., membrane characteristics, catholyte composition, current density and pH on the current efficiency) becomes necessary. During typical membrane electrolysis (Figure 1A) [1] the efficiency of the cathodic process (i.e., hydrogen evolution) is nearly 100%, whereas that for sodium hydroxide is lower and depends on the properties of the membrane. This phenomenon is caused by the flow of a portion of OH^- ions from the anolyte to the catholyte, partially contributing to the total transfer of electric charge through the membrane. Considering the basic assumptions of this process, any flow of OH^- ions through the membrane is undesired because it reduces the NaOH current efficiency and, furthermore, it shortens the coating life of the activated anode as a result of alkalization of the membrane adjacent to the anolyte layer.

Partial flow of anions through the membrane (commonly known as 'backmigration') depends on their nature and the properties of the membrane. The most intensive is the backmigration of OH^- ions [3, 4]. Consequently, if sodium or potassium hydroxide obtained by the membrane method is to be used for the synthesis of salts with anions of a mobility lower than that of OH^- ions, it may appear that it is much more advantageous to obtain the salt in the cathode compartment of the membrane cell. Such a single-stage process shows greater advantage than the process which involves the synthesis of sodium hydroxide in a cell, and its subsequent conversion into the targeted salt in a separate reaction vessel, due to: (i) higher current efficiency of the sodium compound, (ii) lower equipment cost, and (iii) lower voltage on the cell terminals because

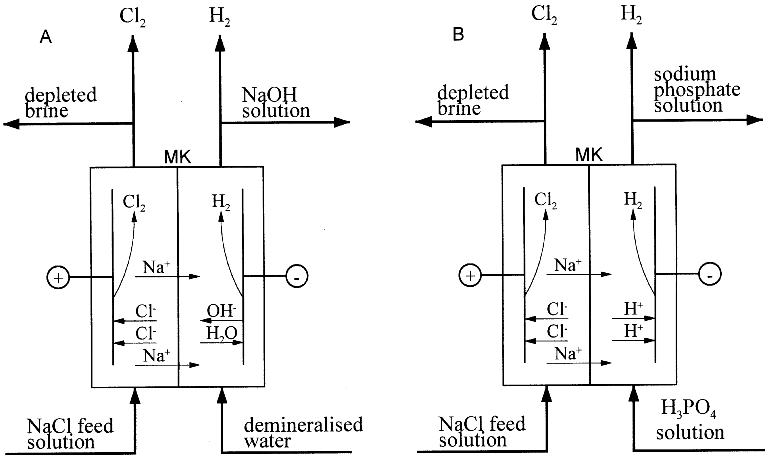

Fig. 1. The principle of membrane electrolysis. Key: (A) when obtaining chlorine, hydrogen and NaOH solution; (B) when obtaining chlorine, hydrogen and sodium phosphate solution; and (MK) cation-exchange membrane.

of the hydrogen evolution potential being, according to Nernst formula, dependent on pH, and increasing (becoming less negative) with decrease in pH. That is,

$$E_{H_2} = \frac{RT}{nF}\ln[\mathrm{H}^+] \cong 0.058 \times (\mathrm{pH}) \tag{1}$$

However, the gain in electric energy saved using this method may be reduced, or totally eliminated, if the electric conductivity of sodium salt solution is lower than that for NaOH optimum concentration solution.

References to sodium or potassium salt synthesis in the membrane cell cathode compartment are scarce and the majority of papers relate to potassium carbonate synthesis [4–6]. The authors concentrate on the determination of an overall current efficiency, ignoring the issue of current distribution in various areas of the cathode compartment. The flat and high compartment cannot be considered as a perfectly-mixed reactor. If water is supplied to the compartment (Figure 1A), then the entire content of the compartment becomes alkaline and backmigration of the OH$^-$ ions is possible everywhere. Nevertheless, the spatial distribution of various concentration of NaOH in various areas is not uniform. If acid is supplied to the cathode compartment (Figure 1B), then the acid reaction prevails in its bottom part and the OH$^-$ ion concentration is slightly lower there. The longer the distance from the area of acid supply the higher the pH, and the participation of OH$^-$ ion migration in the electric charge transfer through the membrane increases.

The present paper contains the results of studies on sodium phosphates electrosynthesis and describes an attempt to assess the influence of pH, as a measure of phosphoric acid conversion, on the current efficiency.

2. Experimental details

A schematic drawing of the experimental plant is presented in Figure 2. The membrane cell consisted of two compartments: anode **2** and cathode **3**, separated by a cation-exchange membrane **4** of surface area 200 cm^2 (5 cm × 40 cm). The anode was made of titanium wire net, cut and stretched, with TiO$_2$ + 40% RuO$_2$ active coating, whereas the cathode was of CrNi acid resistant steel net. The distance between the active surface areas of the electrodes was about 3 mm. The elements of the cells were joined with metal strips and contraction bolts to form a single unit which ensured tightness of the whole assembly and allowed for easy dismantling and membrane replacement.

Nafion® DuPont membranes of types N-423, N-901 and N-961 were used. The N-423 single-layer membrane enables one to obtain 10% NaOH solution at current efficiency of 80 to 92%; N-901 and N-961 are double-layer membranes designed to obtain 32 to 35% NaOH solution at a current efficiency of 95 to 95.5%.

The electrolysis process was conducted at a temperature of 75 ± 2 °C, at a specific current density (per unit of membrane surface) of $j_{\mathrm{m}} = 2$, 3 and 4 kA m^{-2}.

The brine (sodium chloride solution), with concentration of 302 ± 2 g dm^{-3} NaCl and pH 2.2–2.5, free of multivalent ions, was purified using the hydroxide–carbonate method and then on Duolite C-467 ion-exchange resin, was metered into an anode compartment by means of a peristaltic pump **5** at such a rate as to obtain a decrease in sodium chloride solution concentration of 25–30 g dm^{-3} NaCl. Depleted brine and gaseous chlorine flowed out into phase separator **6**. From there, chlorine-containing brine was drained into tank **7**. Gaseous chlorine flowed from separator **6** and tank **7** through a packed column **8** sprayed with 20% NaOH solution. The absorption solution, which contained sodium chloride and hypochlorite was drained into tank **10**.

The catholyte circuit included: cathode compartment **3**, phase separator **11**, where solution samples were taken, intermediate tank **12** and peristaltic pump **13**. Prior to the beginning of each electrolysis cycle the system was filled with *o*-phosphoric acid of concentrations from 1 to 2.25 mol dm^{-3} (from about 10 to 20% H$_3$PO$_4$). Pumps **5** and **13** were started while direct

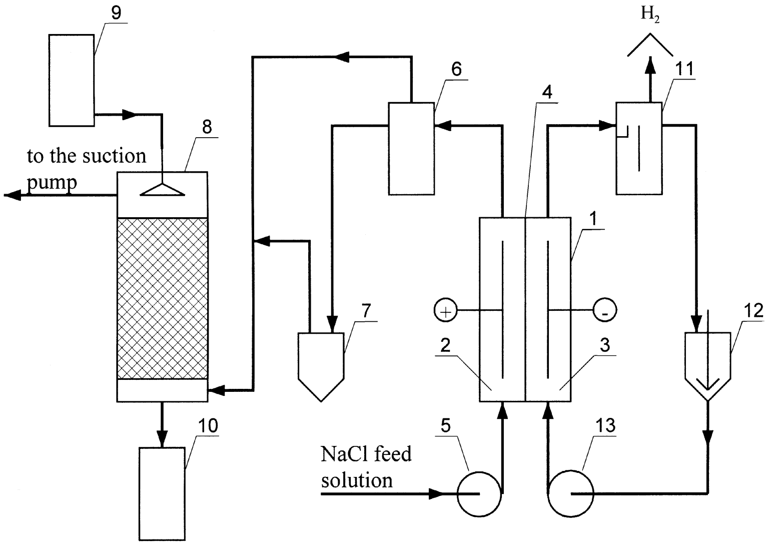

Fig. 2. Schematic diagram of the experimental plant. Key: (1) membrane cell; (2) anode compartment; (3) cathode compartment; (4) cation-exchange membrane; (5) anolyte metering pump; (6) anolyte phase separator; (7) depleted brine tank; (8) packed column for chlorine absorption; (9) tank for 20% NaOH; (10) tank for NaClO + NaCl solution; (11) catholyte phase separator; (12) catholyte intermediate tank; and (13) catholyte metering pump.

current was switched on to supply the electrolysis cell 1. The catholyte began to circulate in the system **3** → **11** → **12** → **13** → **3**···. During electrolysis, as a result of Na^+ ions passing from anolyte to catholyte and due to discharging an equivalent amount of hydronium ions on the cathode, acid was gradually neutralised. On the basis of analytically determined composition of the solution in tank **12** and the phase separator **11**, an instantaneous composition of the catholyte was determined, pH was measured and the current efficiency was calculated corresponding to the determined variation range of solution composition.

Concentrations of individual phosphates and phosphoric acid were determined by acid–base titration in the presence of appropriate indicators.

It was found that NaH_2PO_4 solutions show pH 5.3–5.4 (depending on concentration), whereas Na_2HPO_4 and Na_3PO_4 solutions had pH 9.5–9.6 and 11.1–11.2, respectively.

The method used to determine the current efficiency at relatively low, but precisely specified concentration gradients, constitutes a delayed version of the typical phosphoric acid neutralization process of an industrial cell (in which neutralization is performed in a single flow cycle). Thanks to this delayed neutralization, it is possible to evaluate the changes in current efficiency as the neutralization process progresses.

3. Results

The dependencies of current efficiencies on the initial concentration of phosphoric acid c_p, current density j_m,

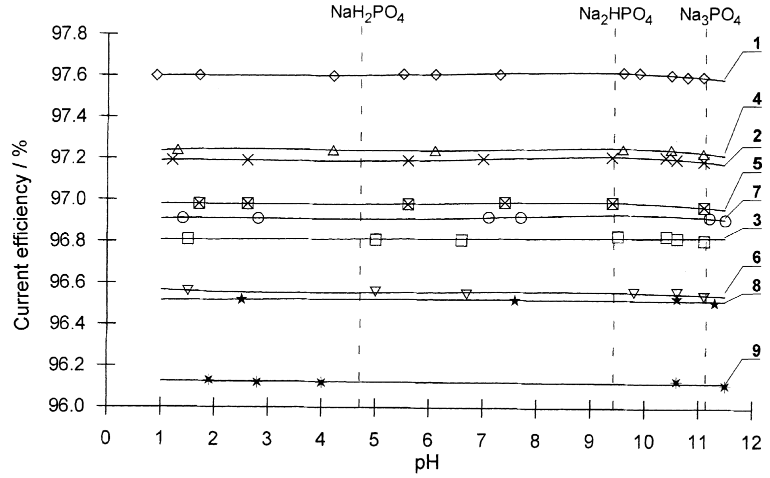

Fig. 3. Synthesis of Na_3PO_4 with N-423 membrane. Dependence of Na_3PO_4 current efficiency on initial phosphoric acid concentration (c_p), current density (j_m) and pH. Key (c_p/M, j_m/kA m^{-2}), respectively: **1** (1.95, 2); **2** (1.96, 3); **3** (1.96, 4); **4** (1.50, 2); **5** (1.48, 3); **6** (1.49, 4); **7** (1.07, 2); **8** (1.07, 3); **9** (1.06, 4).

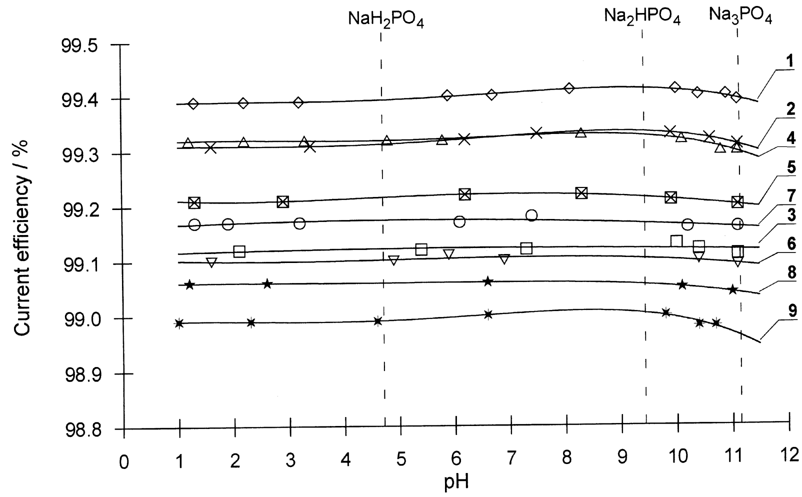

Fig. 4. Synthesis of Na_3PO_4 with N-901 membrane. Dependence of Na_3PO_4 current efficiency on initial phosphoric acid concentration (c_p), current density (j_m) and pH. Key (c_p/M, j_m/kA m^{-2}), respectively: **1** (1.91, 2); **2** (1.94, 3); **3** (1.91, 4); **4** (1.50, 2); **5** (1.47, 3); **6** (1.44, 4); **7** (1.04, 2); **8** (1.03, 3); **9** (1.04, 4).

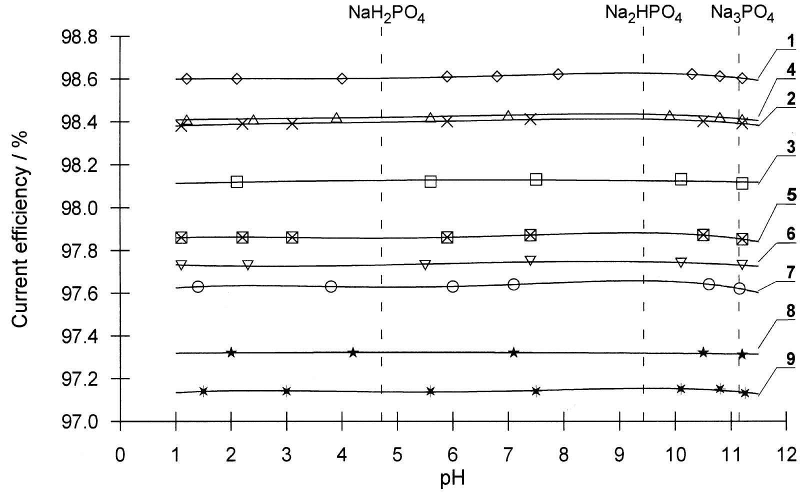

Fig. 5. Synthesis of Na_3PO_4 with N-961 membrane. Dependence of Na_3PO_4 current efficiency on initial phosphoric acid concentration (c_p), current density (j_m) and pH. Key (c_p/M, j_m/kA m^{-2}), respectively: **1** (1.98, 2); **2** (2.01, 3); **3** (2.01, 4); **4** (1.57, 2); **5** (1.60, 3); **6** (1.56, 4); **7** (1.08, 2); **8** (1.07, 3); **9** (1.07, 4).

pH and cation-exchange membrane properties are presented in Figures 3, 4 and 5. The terminal voltages of the cell at the moment of obtaining the phosphate of the given composition are shown in Table 1.

The lowest current efficiencies for sodium hydroxide production (in the electrolysis process aimed at obtaining this compound) were observed when single layer N-423 membrane was used (from 80 to 93% depending on electrolysis conditions), whereas much higher efficiencies were obtained with N-901 and N-961 membranes, which were specially fitted for this very process (from 95.3 to 95.5%) [1, 3]. In the case of N-423 membrane usage, the terminal voltage of the cell was lower by 0.1–0.2 V than in the case of N-901 and N-961 membranes, which corresponds to 2.5–4.0% of the terminal voltage. Thus, it is obvious,

Table 1. Voltage on the membrane cell terminals under the conditions of the electrosynthesis of sodium phosphates
Starting phosphoric acid concentration c_p = 1.91–2.01 mol dm^{-3}.

Cation-exchange membrane	Sodium phosphate obtained	Cell terminal voltage/V at different current density		
		2 kA m^{-2}	3 kA m^{-2}	4 kA m^{-2}
N-423	Na_3PO_4	4.2	4.9	5.6
	Na_2HPO_4	4.1	4.7	5.2
	NaH_2PO_4	4.0	4.5	5.1
N-901	Na_3PO_4	4.9	5.5	6.3
	Na_2HPO_4	4.7	5.3	6.0
	NaH_2PO_4	4.6	5.1	5.7
N-961	Na_3PO_4	4.8	5.4	6.1
	Na_2HPO_4	4.6	5.2	5.9
	NaH_2PO_4	4.5	5.0	5.6

Table 2. Specific consumption of electric energy under the conditions of trisodium phosphate synthesis (Na_3PO_4)
Starting phosphoric acid concentration $c_p = 1.91$–2.01 mol dm^{-3}.

Cation-exchange membrane	Specific electric energy consumption, kWh kg^{-1} Na_3PO_4 at different current densities		
	2 kA m^{-2}	3 kA m^{-2}	4 kA m^{-2}
N-423	2.11	2.47	2.84
N-901	2.42	2.71	3.12
N-961	2.39	2.69	3.05

that the specific electric energy consumption Z_j is given by

$$Z_j = \frac{E_z}{m_h W_p} \qquad (2)$$

where Z_j is the specific electric energy consumption (kWh kg^{-1}, E_z is the cell terminal voltage (V), m_h is the electrochemical equivalent (g A^{-1} h^{-1}), and W_p the current efficiency (a proper fraction).

The N-423 membrane cannot be compared with N-901 or N-961 membranes. Moreover, the N-423 membrane is not designed to obtain 32–35% NaOH solution but only 10% concentration [1].

When the sodium phosphates were obtained, the current efficiencies of these products were higher with all those three membranes studied in relation to NaOH, and the differences among these membranes are much smaller. Depending on electrolysis conditions, concentrations of 96.0 to 97.6% (Figure 3) with N-423 membrane, 99.0 to 99.4% (Figure 4) with N-901 membrane and 97.0 to 98.6% (Figure 5) with N-961 membrane were obtained. The differences do not exceed 3% under comparable conditions.

In the chain of reactions (H_3PO_4) → NaH_2PO_4 → Na_2HPO_4 → Na_3PO_4 a slight decrease in current efficiency was observed not earlier than at the stage of Na_2HPO_4 → Na_3PO_4, which were undoubtedly as a result of some degree of catholyte alkalisation. However, it does not usually exceed 0.05% and may be neglected. What remains difficult to explain is the slight increase in current efficiency (usually less than 0.02%) at the NaH_2PO_4 → Na_2HPO_4 stage. This could be as a result of the mass transfer conditions in the catholyte system.

During the sodium phosphates synthesis, as phosphoric acid was gradually neutralized, the electrical conductivity of the catholyte decreased. This led to an increase in the terminal voltage of the cell. The effect was the least visible one in the case of the N-423 membrane, whereas it was most visible in the case of the N-901 membrane. Voltage differences, usually ranging from 0.5 to 0.7 V, corresponding to about 8–12% of the absolute voltage.

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