Electrosynthesis of Methanolates
by Membrane Electrolysis

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The production of sodium methanolate by membrane electrolysis in the system NaCl|
Nafion membrane|NaOMe has been investigated. The current efficiency exceeds 85%
only in the first stage of the process. The main factors depressing CE are the protons
produced in the anolyte compartment by the oxidation of methanol. The high electroos-
motic flow of methanol (8–11 moles per faraday) reduces the increase of methanolate
concentration, especially at high concentrations of catholyte.

Key words: synthesis, membrane electrolysis, electroosmosis

Because of high permselectivity and stability in corrosive media the perfluori-
nated ion-exchange membranes find many applications as separators in aqueous
solutions. The most important is the chlor-alkali electrolysis [1] described by:

$$H_2O + NaCl \rightarrow NaOH + 0.5H_2\uparrow + 0.5Cl_2$$
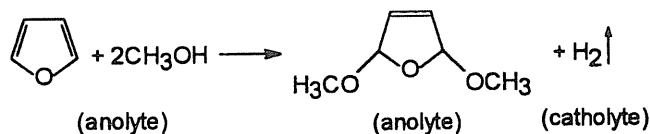(catholyte) (anolyte)   (catholyte)   (anolyte)
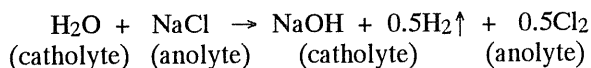
Comparing to the earlier asbestine and mercuric methods the use of membranes is
more economic and protects the environment against the hazardous waste. The use
of membranes in non-aqueous media is as yet limited to the laboratory stage. The
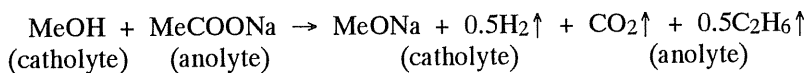examples of electrochemical synthesis with an ion-exchange membrane as separator
are:
– electrochemical hydrogenation of olefinic double bonds [2]:

$$RCH=CHR' + H_2O \rightarrow RCH_2CH_2R' + 0.5O_2\uparrow$$
(catholyte)   (anolyte)   (catholyte)   (anolyte)
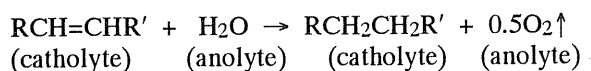
– dimethoxylation of furan and other compounds [3,4]:

– electrosynthesis of alkali alcoholates [5]:

$$MeOH + MeCOONa \rightarrow MeONa + 0.5H_2\uparrow + CO_2\uparrow + 0.5C_2H_6\uparrow$$
(catholyte)   (anolyte)   (catholyte)   (anolyte)

The advantage of introducing ion-exchange membranes is the elimination of supporting electrolyte and, consequently, simplified product purification. The reaction, in which sodium methanolate is produced, differs from that of chlor-alkali electrolysis in the use of sodium acetate instead of sodium chloride. In this reaction Hamann *et al.* using Nafion 214 membrane attained the current efficiency exceeding 80% during a 2 h process [5]. However, since sodium acetate is not as cheap as sodium chloride, the application of this compund is of limited practical importance.

In this paper the performance of electrosynthesis of sodium methanolate using sodium chloride as the anolyte electrolyte is examined. The reaction giving the desired product is the same as in the chlor-alkali electrolysis:

$$\text{MeOH} + \text{NaCl} \rightarrow \text{MeONa} + 0.5\text{H}_2\uparrow + \text{Cl}_2\uparrow$$
(catholyte) (anolyte)　　　 (catholyte)　　 (anolyte)
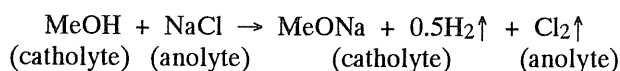
As previous investigations have shown, the perfluorinated Nafion membranes exhibit good transport properties in methanolic solutions [6,7,8]. The conductivity in $\text{NaCl}_{\text{MeOH}}$ is about 2 times lower than that in NaCl_{aq}, the transport number of Na^+ is above 0.9, in NaOMe solutions (T = 25°C) the conductivity attains 1000 S/m^2 (N417), for N901 reaches even 1800 S/m^2 against 3300 S/m^2 (maximum) in 4 M NaOH_{aq} (T = 22°C [9]). The permeability coefficient of electrolyte ranges from $2 \cdot 10^{-7}$ (N901) to $2.5 \cdot 10^{-7}$ (N417) m/s and is even lower than that for Nafion 120 in NaOH solutions ($5 \cdot 10^{-7}$ m/s [10]). Thus, the back diffusion should not be significant in electrolysis of methanolates. Other parameters, such as the electroosmotic and osmotic flow of MeOH, the oxidation of MeOH in the anolyte, which are expected to affect the electrolysis, will be discussed below.

EXPERIMENTAL

The reinforced Nafion membranes were selected – the one-layer sulfonate Nafion 417 and the two layer Nafion 901 consisting of sulfonate and carboxylate layers. The membranes were boiled for an hour in methanol and then stored in *ca.* 0.1 m NaCl methanolic solution.

The sodium chloride p.a. was heated in 400°C before use. The solutions of NaOMe were prepared by dissolving sodium in p.a. MeOH.

The electrolysis was carried out in a thermostated glass cell. Each half-cell (vol. 250 cm^3) was equipped with a magnetic stirrer and connected through the condenser with an air-burette to control the gas evolution. The active surface of membrane was 6.2 cm^2. The electrodes (anode – Pt wire net, cathode – Pt coated titanium) were placed in about 1 cm distance from the membrane surface.

To examine the current efficiency of the process, three samples of catholyte were taken every 20–30 min and the catholyte was weighed before and after electrolysis. Additionally, the samples of anolyte were taken to determine the concentration of Na$^+$ and H$^+$ ions. The concentration of H$^+$ and MeO$^-$ were determined by titration. The concentration of Na$^+$ ions was determined by the atomic absorption spectrometry (Varian 20ABQ).

Because of the low solubility of NaCl in MeOH the electrolysis was always carried out in an excess of undissolved NaCl. Two current efficiencies (*CE*) were calculated:

1) *CE(mean)* – the mean in the interval 0 – t_i:

$$CE(mean) = F \frac{\Delta n_2(t_i)}{It_i} = \frac{F}{It_i}\left(m_i c_i + \sum_{j=1}^{i-1} m_{sa,j}\, c_j - m_0 c_0 \right) \tag{1}$$

2) *CE(diff)* – differential – the mean in the interval $t_{i-1} - t_i$:

$$CE(diff) = F\frac{\Delta n_2(t_i) - \Delta n_2(t_{i-1})}{I(t_i - t_{i-1})} = \frac{F}{I(t_i - t_{i-1})}\left(m_i c_i - (m_{i-1} - m_{sa,i-1})c_{i-1}\right) \quad\quad (2)$$

In above equations $\Delta n_2(t_i)$ denotes the increase of methanolate ions in the catholyte in the interval $0 - t_i$, $m_{sa,i}$ — the mass of sample taken at t_i, I — current, F — Faraday constant.
The mass of catholyte in t_i, m_i, was calculated from the formula:

$$m_i = m_0 + \frac{m_{end} - m_0}{t_{end} - t_0}t_i - \sum_{j=1}^{i-1} m_{sa,j} \quad\quad (3)$$

Since it was impossible to determine m_i during the electrolysis, the linear increase of m_i in formula (3) was assumed. The final mass of catholyte, m_{end}, was calculated as the sum of the mass measured after electrolysis, m'_{end}, and of the samples, $m_{sa,i}$:

$$m_{end} = m'_{end} + \sum_{i=1}^{n} m_{sa,i} \quad\quad (4)$$

For convenience, the concentrations in this paper are expressed in moles per kilogram of a solution, unless otherwise stated. The auxiliary measurements of osmotic flow in the system sat.NaCl|N417| NaOMe were performed in the electrolysis cell, equipped with capillary to measure the volume changes of catholyte. The measurement of solubility of NaCl in methanol was performed in a stirred thermostated cell.

RESULTS AND DISCUSSION

The electrolysis was performed in two systems — saturated NaCl|Nafion 417| NaOMe and in NaOMe|Nafion 417|NaOMe, as reference system. The conditions of electrolysis were: constant current 0.7 A (1.1 kA/m^2), concentration of NaOMe — 0.68, 1.3, 2.5 (in moles per kg solution), temperature — 28–30°C. At lower current density (0.74 kA/m^2) the lower efficiencies were observed. After preliminary experiments the membrane N901 was excluded because of delamination (the creation of bubbles on the membrane surface). This effect was also observed during the membrane electrolysis of aqueous solutions of KOH [11]. Generally, the electrolysis is described by the current efficiency, proportional to the number of moles of produced component ((1)), the increase of concentration of that product, and the energetic losses. Here, only the first two quantities will be discussed in detail. The system was not optimized in respect to the reduction of potential drop on the electrodes (distance, area of electrodes, temperature).

The schema of transport: To discuss the results in detail, the schema of transport presented in Fig. 1 have been assumed.

As the pH of anolyte decreases in time (Fig. 2), it has been assumed that only Na$^+$ and H$^+$ cations migrate across the membrane, i.e.

$$\bar{t}_{Na^+} + \bar{t}_{H^+} = 1 \quad\quad (5)$$

The H$^+$ ions neutralize the MeO$^-$ ions moving towards anode either in the membrane or near the membrane interface with catholyte, depending on the concentrations of these ions.

a)

MEMBRANE

$\bar{t}_{Na^+}$ Na$^+$

$(1-\bar{t}_{Na^+})$ H$^+$

MeO$^-$

MeOH

$\bar{t}_0$ MeOH

J_{osm} MeOH

J_{dif} NaOMe

$\frac{1}{2}$H$_2$ e

MeO$^-$

MeOH

ANOLYTE
sat. NaCl/MeOH

CATHOLYTE
NaOMe/MeOH

b)

MEMBRANE

$\bar{t}_{Na^+}$ Na$^+$

$(1-\bar{t}_{Na^+})$MeO$^-$

$\bar{t}_0$ MeOH

$\frac{1}{2}$H$_2$ e

MeO$^-$

MeOH

ANOLYTE
NaOMe/MeOH

CATHOLYTE
NaOMe/MeOH
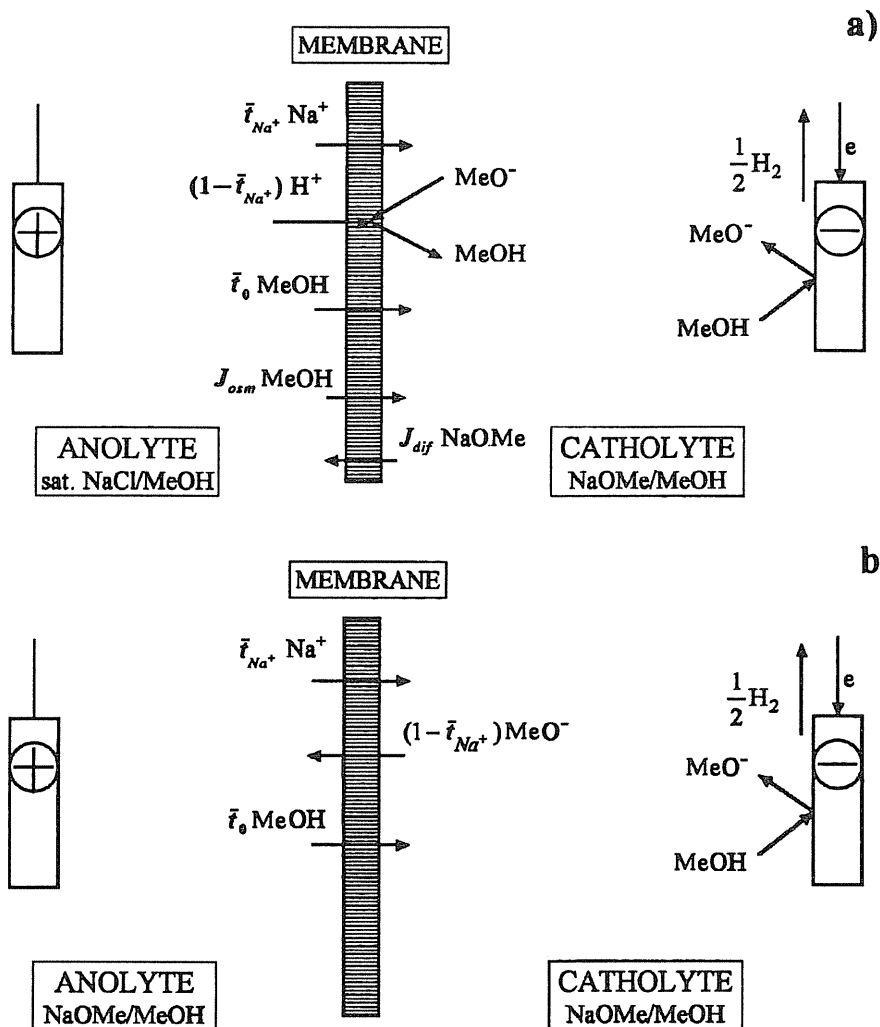
Figure 1. Fluxes in the system: a) NaCl|N417|NaOMe, b) NaOMe|M|NaOMe; only the cathode reaction is shown.

The source of H$^+$ ions in anolyte is the oxidation of MeOH on the anode, favoured by the low solubility of NaCl in MeOH ($<$ 14 g/kg of solution [12] in comparison with 360 g/kg in aqueous solution [13]) reducing the limiting current. As mentioned in EXPERIMENTAL, to keep the concentration of NaCl at the highest possible level, the electrolysis was always conducted with an excess of undissolved NaCl.

Theoretically, the rate of removal of Na$^+$ ions from anolyte is $dc/dt = (I/F)/m_{Anol}$ = $3.5 \cdot 10^{-5}$ mol/kg·s (assuming $\bar{t}_{Na^+}$ = 1), whereas the rate of dissolving of NaCl in the solution of concentration c = $0.8c_{max}$ is $25 \cdot 10^{-5}$ mol/ kg·s (Fig. 3). This rate decreases with concentration to *ca.* $4.5 \cdot 10^{-5}$ mol/ kg·s at $0.95c_{max}$. In spite of higher
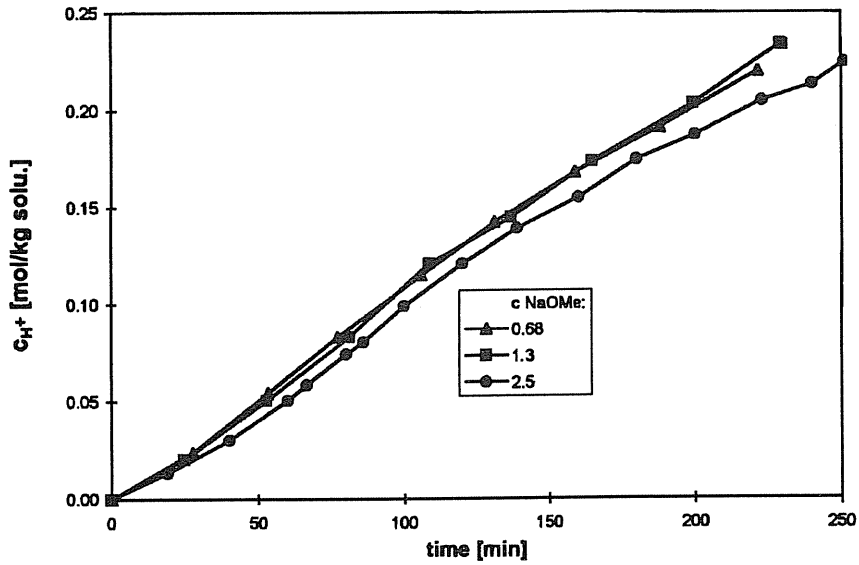
Figure 2. Concentration of H⁺ ions in anolyte *vs.* time of electrolysis.

rate of dissolving, the decrease of the concentration of Na⁺ ions in anolyte proceeds and after about 150 min reaches the limit of 50–75% of c_{max} (Fig. 4). It means that in the solution saturated with Cl_2 and containing H⁺ ions the solubility of NaCl is even lower than in a pure solution.
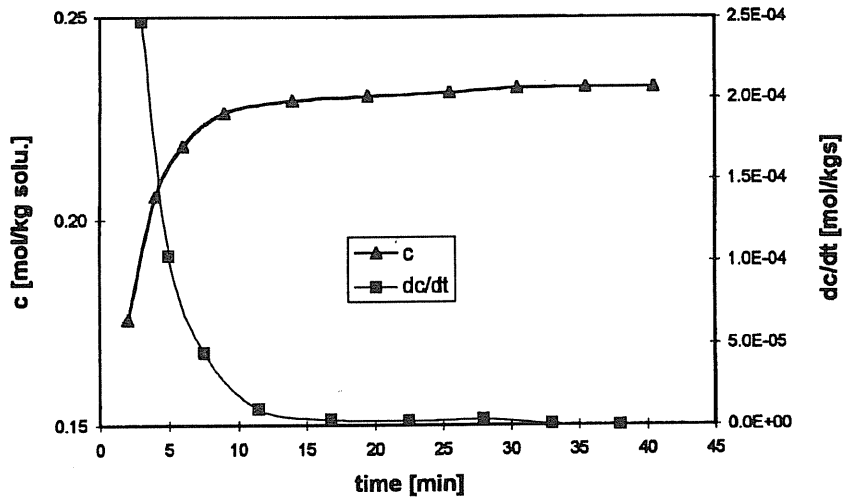

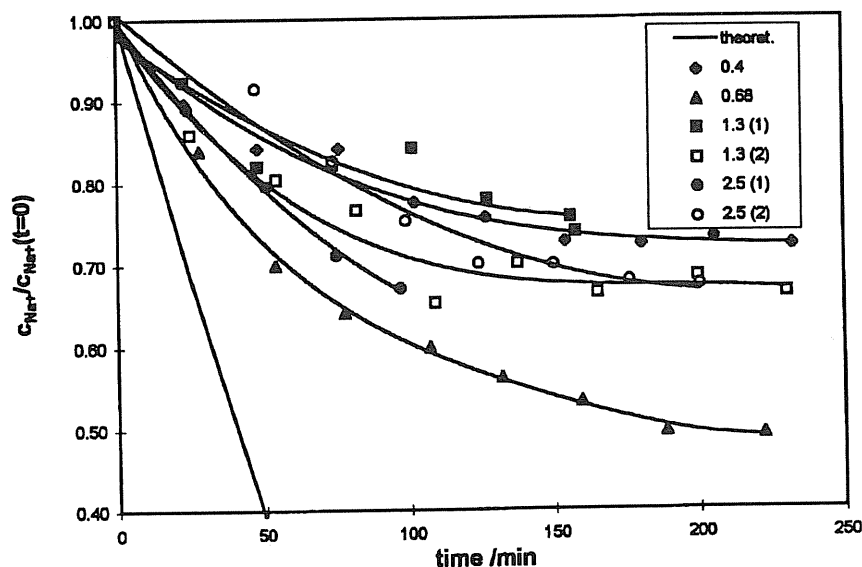**Figure 3.** Solubility of NaCl in MeOH; T = 25°C.

Figure 4. Relative concentration of Na⁺ ions in anolyte *vs.* time of electrolysis; the numbers in parenthesis denote different runs of electrolysis.

The current efficiency: The changes of current efficiencies *CE(mean)* and *CE(diff)* during the electrolysis are presented in Fig. 5.

In the system with saturated NaCl as anolyte the efficiency is high only in the first hour of electrolysis. Then *CE* decreases (*CE(diff)* even below 40%) for all concentrations of catholyte. Instead, in the system NaOMe|N417|NaOMe the current efficiency is almost time independent. However, the efficiency is not as high as in the system with NaCl. This difference, especially seen at high concentration of NaOMe, means that the state of the membrane is determined by the anolyte, *i.e.* with NaCl as anolyte the membrane is not invaded by MeO⁻ anions and the transport number of sodium ions is higher. According to the schema in Fig. 1a the change of number of moles of NaOMe, Δn_2, is given by:

$$\Delta n_2 = \bar{t}_{Na^+}\frac{It}{F} - J_{dif}S_m t \tag{6}$$

Substitution of (6) into (1) yields a known formula for *CE* [14]:

$$CE = \bar{t}_{Na^+} - J_{dif}S_m F/I \tag{7}$$

which relates *CE* to the transport number of Na⁺ and diffusional flux of methanolate, J_{dif}. The sign of J_{dif} is positive when directed to the anolyte. Using diffusion data of NaOMe to MeOH [8] it has been calculated that the negative effect of diffusion is low – it does not ecced 0.04 mol/F for the concentration of NaOMe up to 2.5 m. Thus,
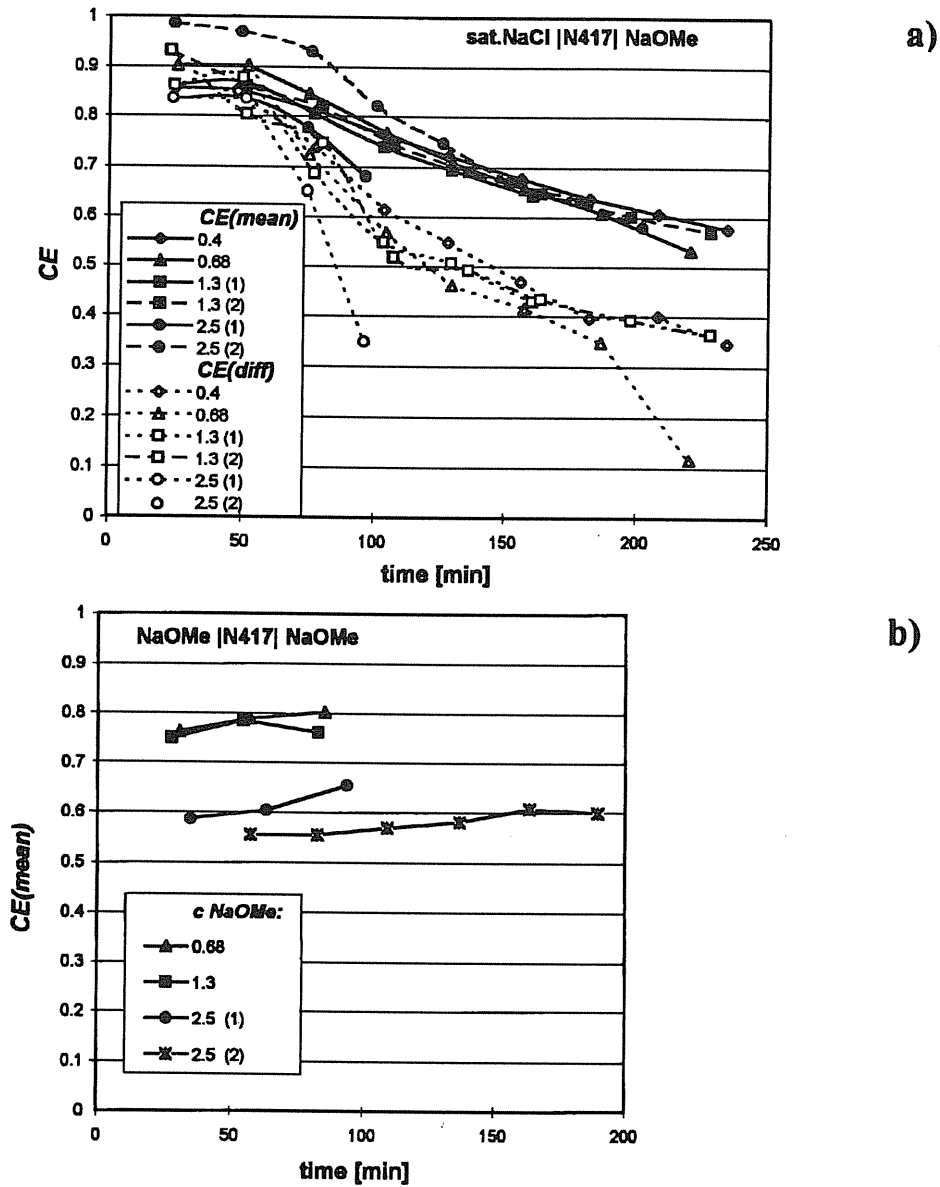
Figure 5. Mean and differential current efficiency vs. time of electrolysis for different concentrations of catholyte (NaOMe) in the system: a) sat.NaCl|N417|NaOMe, b) NaOMe|N417|NaOMe; the numbers in parenthesis denote different runs of electrolysis.

CE can be identified directly with $\bar{t}_{Na^+}$ and, according to (5), the main factor diminishing CE is the increase of transport number of H^+ ions. This fact is supported by the similar CE observed for different concentrations of NaOMe (Fig. 5a).

To check the schema of fluxes presented in Fig. 1, the transport number of Na^+ has been calculated using the experimentally determined changes of catholyte concentration, Δc_{cat}, and the changes calculated from (9), $\Delta c_{cat,apr}$. The square function of $\bar{t}_{Na^+}$ vs. time has been assumed:

$$\bar{t}_{Na^+} = a_0 + a_1 t + a_2 t^2 \tag{8}$$

The a_i coefficients of (8) have been calculated minimizing the square deviation $(\Delta c_{cat} - \Delta c_{cat,apr})^2$. The calculated $\bar{t}_{Na^+}$ is close to the experimental CE (Fig. 6) thus confirming the validity of the assumed schema of transport processes.
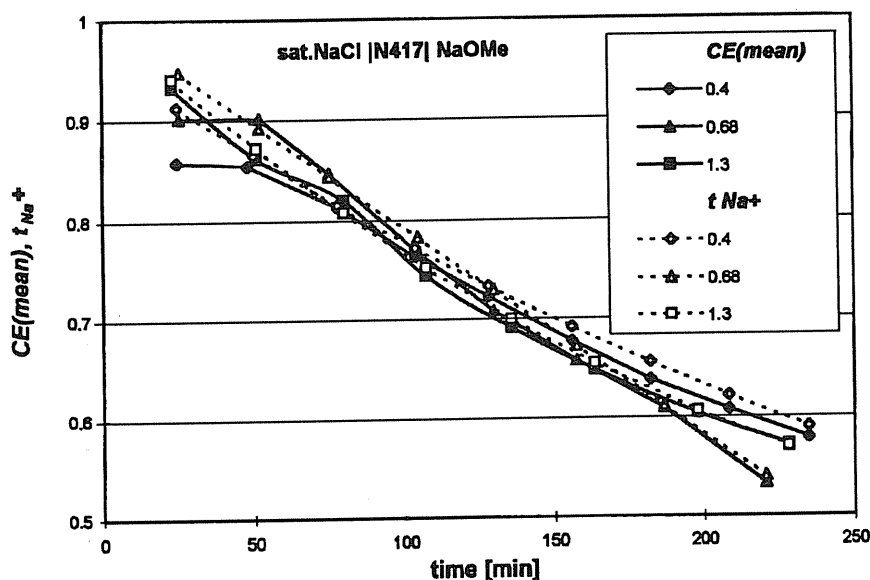

Figure 6. Comparison of experimental CE with $\bar{t}_{Na^+}$ calculated assuming the schema of fluxes shown in Fig. 1a.

The concentration and mass of catholyte: The changes of catholyte concentration in both systems, expressed as $c(t) - c(0)$, are shown in Fig. 7a,b. They correspond to the changes of current efficiency (Fig. 5). In the system sat.NaCl|N417|NaOMe $c(t) - c(0)$ initially is large, then it is smaller and smaller and can attain negative values for high starting concentrations of catholyte. On the other hand, in the system NaOMe|N417|NaOMe the increase of concentration is linear with time (Fig. 7b) which indicates that the transport number of Na^+ is approximately constant. The reason for this is the lack of H^+ ions which, when produced, are immediately neutralized by OMe^- ions.

To discuss $c(t) - c(0)$ in detail the reference to the general formula should be made:

$$c(t) - c(0) = \Delta c = \frac{n(0) + \Delta n}{m(0) + \Delta m} - \frac{n(0)}{m(0)} = \frac{\Delta n - c(0)\Delta m}{m(0) + \Delta m} \tag{9}$$
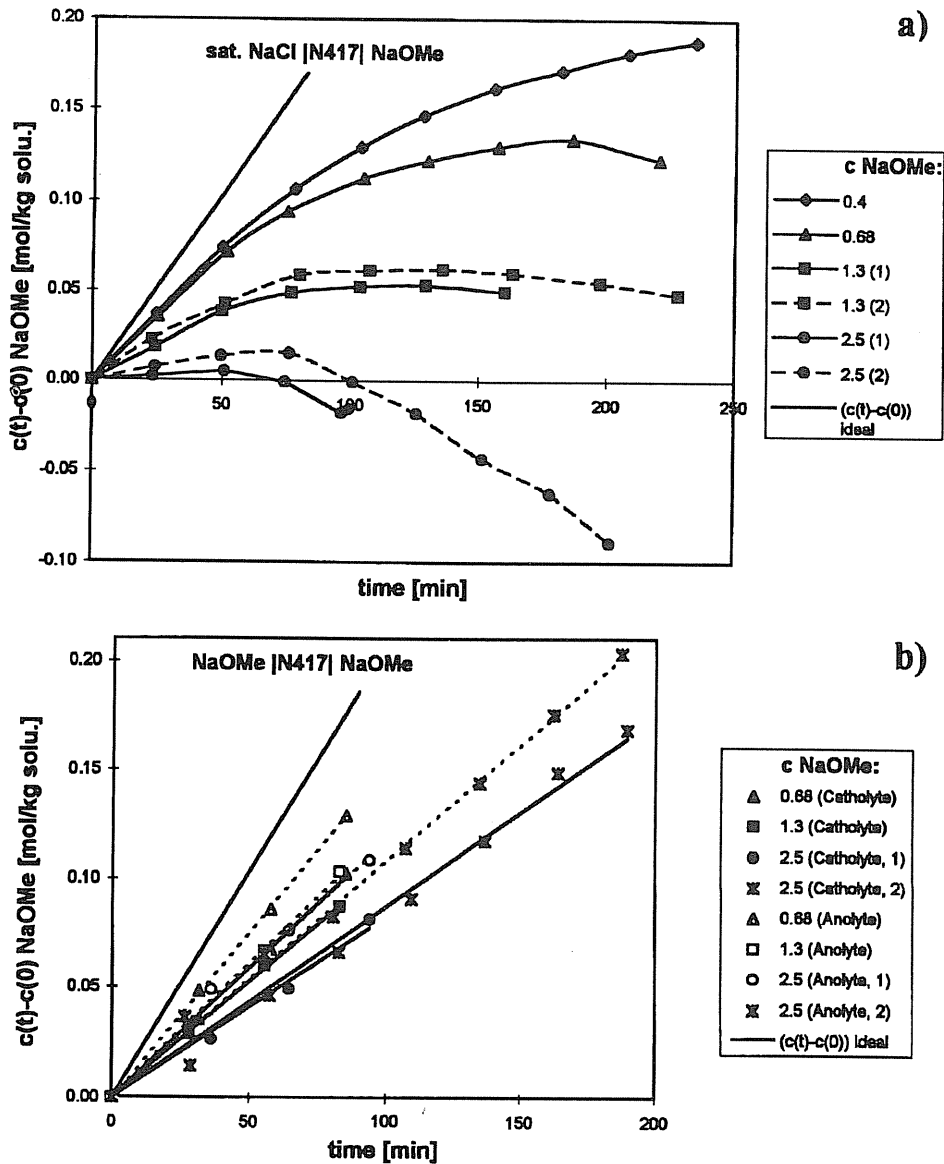
Figure 7. The increase of concentration of NaOMe for different concentrations of catholyte (NaOMe) in the system: a) sat.NaCl|N417|NaOMe, b) NaOMe|N417|NaOMe; the numbers in parenthesis denote different runs of electrolysis.

where $c(t)$, $n(t)$, $m(t)$ denote concentration, number of moles of solute and mass of the solution at time t, respectively. From (9) it is seen that Δc is determined by Δn as well as by Δm. According to the schema in Fig. 1a the total change of catholyte mass per 1 F, Δm_{cat} (Fig. 8) is expressed as a sum of the following components: the changes caused by electroosmotic, $\Delta m_{cat,elosm}$ and osmotic, $\Delta m_{cat,osm}$, flow of MeOH, diffu-

a)

NaOMe:

B

(1)

(2)

(1)

(2)

)-c(0))

b)

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sion, $\Delta m_{cat,dif}$, and by the transport of Na^+ and H^+ ions, including the cathode reaction, $\Delta m_{cat,Na\&H}$:

$$\Delta m_{cat} = \Delta m_{cat,elosm} + \Delta m_{cat,osm} + \Delta m_{cat,dif} + \Delta m_{cat,Na\&H} \qquad (10)$$

where

$$\Delta m_{cat,elosm} = \bar{t}_0 M_0 \qquad (11) \qquad \Delta m_{cat,osm} = \frac{F}{I} \rho_0 S_m J_{v,osm} \qquad (12)$$

$$\Delta m_{cat,dif} = -\frac{F}{I} S_m J_{dif} M_s \qquad (13) \qquad \Delta m_{cat,Na\&H} = \bar{t}_{Na} M_{Na} + (1-\bar{t}_{Na}) M_H = \bar{t}_{Na}(M_{Na}-M_H) \qquad (14)$$

The total change of catholyte mass (mean of the values presented in Fig. 8), the components of each flows, and the electroosmotic transport number of MeOH, calculated from (11) are listed in Table 1. Because of negligible effect the diffusion component is not shown (< 0.04 mol/F = 2.2 g/F).

Table 1. The components of change of catholyte mass and the electroosmotic number of MeOH, $\bar{t}_0$, in the system saturated NaCl|N417|NaOMe.

c NaOMe [mol/kg solu.]	0.68	1.3	2.5
Δm_{cat} [g/F]	375.3	348.0	275.1
$\Delta m_{cat,elosm}$ [g/F]	356.4	326.7	251.2
$\Delta m_{cat,osm}$ [g/F]	5.7	8.1	10.7
$\Delta m_{cat,Na\&H}$ [g/F]	13.2	13.2	13.2
$\bar{t}_0$	11.1	10.2	7.8
% elosm.	95.0	93.9	91.3
% osm.	1.5	2.3	3.9
% Na&H	3.5	3.8	4.8

The values of osmotic flow, needed for the calculation of $\Delta m_{cat,osm}$, were 8.55, 12.1 and 16.0 times 10^{-8} m/s for the concentrations 0.68, 1.28 and 2.49, respectively. From the data in Table 1 it is seen, that the predominant component of Δm_{cat} is the electroosmotic flow of MeOH. The electroosmotic transport number of MeOH, $\bar{t}_0$, is much higher than that of water for comparable concentrations of NaOH solutions ($\bar{t}_0$ = 3–6 [10]; in very concentrated solutions, as in the chlor-alkali electrolysis, it decreases to 1–3). This flow hinders the increase of NaOMe concentration, especially at high concentrations (Fig. 9). The electroosmotic transport of MeOH for the system NaOMe|N417|NaOMe has been calculated by

$$\bar{t}_0 = \frac{1}{M_0} \left(\Delta m_{Cat} \frac{F}{It} - \bar{t}_{Na^+} M_s \right) + 1 \qquad (15)$$

(15) results from the mass balance of catholyte (Fig. 1b). As the initial concentrations of anolyte and catholyte are equal, the diffusion and osmotic flows were not taken into account. The calculated values of $\bar{t}_0$ (7.2, 4.8, 2.0 for the concentrations 0.68,
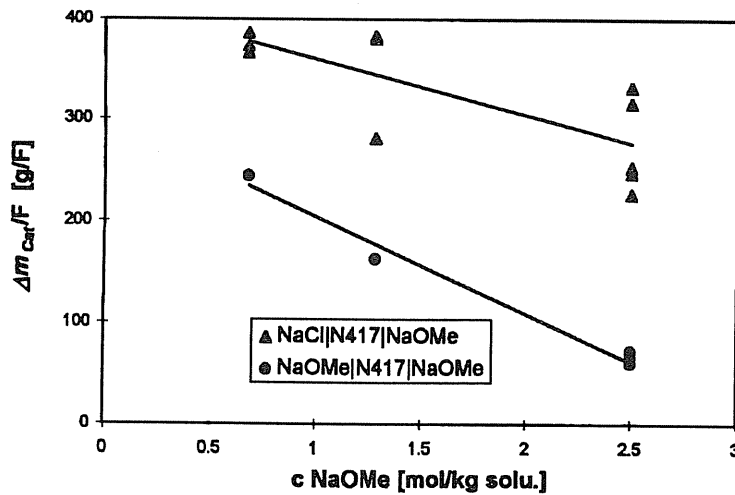
Figure 8. Increase of mass of catholyte per 1 F *vs.* concentration of catholyte.
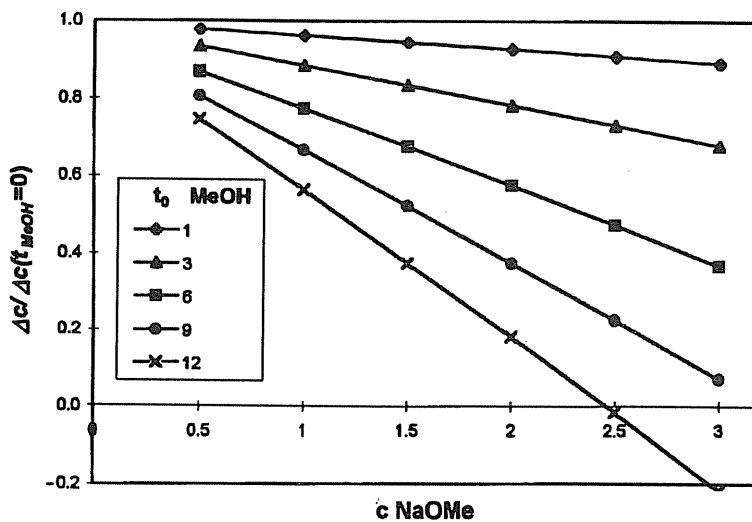

Figure 9. Dependence of relative increase of concentration of catholyte on the concentration of NaOMe and the transport number of MeOH, calculated assuming $\bar{t}_{Na^+} = 1$.

1.3, 2.5, respectively) are lower (see Table 1 and Fig. 8) than those for the system sat.NaCl|N417|NaOMe. This difference again supports the hypothesis that the state of membrane during electrolysis is determined by the anolyte. With NaCl as anolyte the MeO⁻ ions do not enter the membrane and the molecules of methanol receive more momentum from the cations than in the system with NaOMe as anolyte, where a significant electromigration of MeO⁻ ions towards anolyte hampers the electroosmotic flow of MeOH.

CONCLUSIONS

1. The reinforced Nafion membranes are stable in methanol solutions of NaCl and NaOMe during the electrolysis.

2. In the initial stage of electrolysis (*ca.* 1 h) the current efficiency is high (> 85%), however, in further electrolysis the production of protons in anolyte decreases the efficiency even below 40%. The only way to overcome this problem is to change sodium chloride for another type of electrolyte which in the anode reaction would give neutral, but valuable product.

3. At high concentrations of sodium methanolate it is practically impossible to obtain a significant increase of concentration. The reason is a high electroosmotic flow of solvent, which can be only reduced by developing a membrane of reduced swelling in methanol.

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