

# Electrodialysis in a non-aqueous medium: production of sodium methoxide

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## Abstract

A method is described for the production of an alkali alkoxide from an alcohol and a salt by way of electrodialysis. The principle involves the double decomposition of a salt and an alcohol. In effect, an alcohol is split into protons and alkoxide ions, the latter forming the alkoxide with the metal ions of the salt. This finding opens new venues of application and offers opportunities for new chemical processes.

**Keywords:** Electrodialysis; Non-aqueous medium; Sodium methoxide

## 1. Introduction

Alkoxides are important chemical reagents, predominantly being used as condensation agents in organic syntheses and to introduce the alkoxyl group into other compounds [1].

The conventional method of preparation of an alkoxide is to allow the alcohol to react with a metal or its compounds. For instance, sodium alkoxide can be prepared either by reaction of elementary sodium or of sodium hydroxide with alcohol. In the former case, the costs are high due to the high price of the element. In the process also the alcohol will be unnecessarily removed if it is lower boiling or forms a minimum boiling azeotrope with water. Another method is the amalgam process, which is analogous to the alkali chloride electrolysis but is carried out in an alcoholic medium. A further electrolytic method [2] foregoes the use of mercury and employs a cation exchange membrane for the transfer of sodium as ions from the anode chamber to the cathode chamber. In the case of

an acetate suggested as the source for the alkali ion, the anode reaction at the high current densities applied would lead to the formation of ethane and carbon dioxide (Kolbe reaction).



while hydrogen is released at the cathode.

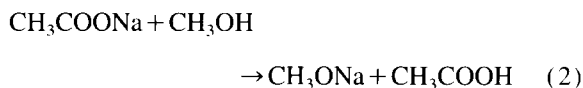
## 2. The principle of the process by electrodialysis

In an electrolytic process a pair of electrodes is needed for each cell. In electrodialysis (ED) a multitude of membranes can be introduced thereby creating an array of cells between the two electrodes.

Moreover, in the electrolytic process mentioned above, the salt used as a source for the alkali ion is converted at the anode into waste gases, viz. ethane and carbon dioxide. This amounts to a constant consumption of the salt. With the help of ED an attempt was made to devise a method to conserve the anion of the

alkali salt by way of double decomposition in all the intermediate cells, allowing for any losses only in the single anode chamber of the ED stack. Therefore, for a large number of cells in a stack the minimal consumption of reactants and production of gases due to electrolysis can be ignored.

The overall reaction for a cell in an ED stack would be:



The acetate ion is recovered as acetic acid and can be reconverted to the salt.

A methanolic solution of sodium acetate (“diluate”) is circulated through the anode chamber; the salt releases the  $\text{Na}^+$  ions (Fig. 1). The latter pass through a cation exchange membrane to enter the adjacent compartment being circulated with methanol (“concentrate” in the “alkoxide cycle” or “alkoxide loop”). This chamber is bordered by the membrane and a further pair of anion and cation exchange membranes as shown in the figure. The  $\text{Na}^+$  ions form the alkoxide with the methanol present. The protons produced in the reaction pass through the latter barrier entering the next “acid chamber” or “acid cycle” or “loop” bordered by the membrane pair and an anion exchange membrane. Sodium acetate solution is introduced in the adjacent compartment (“diluate” or “salt cycle” or “salt loop”), so that the acetate ions, migrating towards the anode, enter the acid chamber containing the protons to form acetic acid. The  $\text{Na}^+$  ions of the salt migrate from the salt compartment towards the cathode and through the next cation exchange membrane to enter the cathode chamber which is fed with the concentrate. Here again the alkoxide is formed but hydrogen is released as such at the cathode.

A common shortcoming of an anion exchange membrane is the fact that it does not efficiently prevent the passage of protons. Due to the proton leakage such a membrane would offer a relative barrier to  $\text{Na}^+$  ions only, acting as a filter and allowing the passage of protons as desired. A typical demerit of an anion exchange membrane is thus used to advantage. The cation exchange membrane of the membrane pair serves in turn as a barrier for the acetate ions. Otherwise, they would migrate towards the anode to pass through the anion exchange membrane and enter the

alkoxide compartment. As a bipolar membrane represents in principle a membrane pair, after runs 1 and 2 the latter was replaced by a bipolar membrane for subsequent runs.

In this set up the three intermediate compartments between the electrode chambers can be considered as a functional cell, needed to produce the acid and the alkoxide. An array of such cells can be introduced between the electrodes as already mentioned.

### 3. Experimental

#### 3.1. Special considerations and precautions

Before beginning the investigation, certain uncertainties had to be faced. As the ion exchange membranes have been developed for applications in aqueous solutions, no information was available on the compatibility of the membranes employed in alcohol. Likewise, no literature was available on electrodialysis in absolutely non-aqueous media.

The stack had been conceived by the manufacturer only for investigations in aqueous media. As a result, also the gaskets, spacers, tubing, etc. had to be replaced by special elements suited to the new medium.

#### 3.2. Experimental set-up and conditions

The salient features of the ED stack are given in Table 1. The fresh membranes were laid in methanol for 24 h at normal temperature before they were mounted into the stack. The membranes ACLE-5P and C66-10F were chosen despite their thickness (0.2–0.35 mm), as they could be expected to be especially resistant in organic media.

The diluate consisted of an 11 wt% sodium acetate solution in methanol. Pure methanol could be used as the concentrate (alkoxide cycle). But to ensure some conductivity in the liquid at the start up of a run, a methanolic solution of 0.5–1.5 wt% sodium acetate (in runs 1 to 3) or sodium methoxide (in run 4) was used. Likewise, for start up, a solution of 1 wt% acetic acid in methanol was employed in the acid chamber of run 1.

In all the runs the EMF across the stack was maintained constant. The temperatures, specific conductivities (in the range 0.2–40 mS/cm), the volume flows

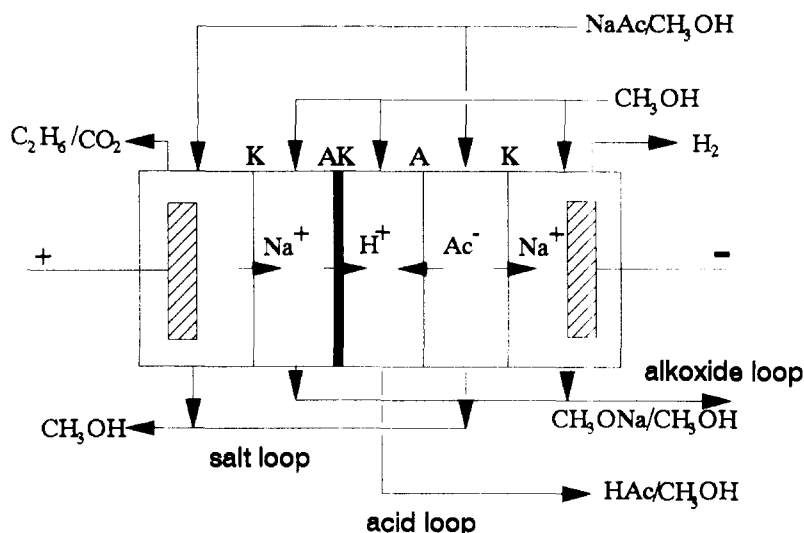


Fig. 1. Electrodialysis cell illustrating the principle of the process; K, cation exchange membrane; A, anion exchange membrane.

in the various loops as well as the varying current strength were observed constantly and registered. The current strength increased with time from around 0.2 to 2–4 A; the values for the current densities given (Table 3) are mean values over the time for the particular run, derived from the total amount of current in A h. calculated for each run.

### 3.3. Analysis

Samples for analysis were taken at the beginning immediately after application of the electric field and again at the end of the run. The contents of NaOH, acetic acid, water and the methoxide were determined potentiometrically. Further, an elementary analysis of sodium and a separate quantitative determination of the acetate by HPLC were carried out. The gas production in the electrodes were not considered to be of vital interest at this stage of the study and were not evaluated.

## 4. Results and discussion

### 4.1. Run 1 with a separate acid cycle (Fig. 1)

For the sake of simplicity of operation the number of cycles (pumps, reservoirs, fittings, etc.) was reduced to a minimum. The diluate was fed from the same reservoir into the anode chamber and the salt chamber. Both the cathode chamber and the alkoxide chambers were fed from the same concentrate reservoir. Only the acid loop had a separate reservoir. The solutions were pumped to the stack and circulated via the reservoirs during the whole run.

In the first run the temperature was maintained at 323 K. An EMF of 100 V was applied arbitrarily, which led to an average current strength of about 2 A. After 71 h 1 mole of the alkoxide was produced in the corresponding cycle (Table 2). There was no build-up of acetic acid in the acid loop. On the contrary, a depletion was observed, with the net amount of acid (0.85 mole)

Table 1  
Technical features of the electrochemical stack

Anode	PT/Ti
Cathode	stainless steel 1.4571
Membranes	cation exchange: C66-10F of Tokuyama Corp. anion exchange: ACLE-5P of Tokuyama Corp. bipolar: Fraunhofer Institut für Grenzflächen- und Bioverfahrenstechnik, Stuttgart
Effective cross-sectional area of membrane	100 cm <sup>2</sup>

Table 2  
Experimental results illustrating the production of alkoxide and acetic acid

Run	Temperature (K)	EMF (V)	Duration (h)	Methoxide produced in alkoxide cycle (mol)	Acetic acid produced (mol)			
					in acid cycle	in salt cycle	in salt/acid cycle	in anode cycle
1	323	100	71	1.06	0.39	1.24		
2	323	100	25	0.59			0.58	
3	323	40	6	0.37			0.43	
4	292	40	5.83	0.19			0.11	0.17

being formed or being accumulated in the salt loop.

This is due to a fast flux of protons through the anion exchange membrane separating the acid and salt compartments (Fig. 1), so that they reach the acetate ions in the salt compartment before the latter could migrate into the acid chamber, thus forming the acetic acid in the salt loop itself.

#### 4.2. Runs 2 to 4 with a combined salt/acid cycle (Fig. 2)

As the results indicated that the acid cycle is superfluous, the salt and acid loops were united to a single loop by removing the anion exchange membrane between them. The acid formed from the salt by protonation was retained in the same loop (run 2).

In the meantime, a special stack was constructed which had the same dimensions but with the width of the compartment reduced from 4.6 to 0.8 mm. The bipolar membrane replaced the membrane pair. The

next runs, 3 and 4, were carried out under these improved conditions. Run 3 could be operated under a mean current strength of 1.3 A. In run 4, a separate cycle was installed for the anode compartment, so as to distinguish between the diluate and the anode cycles.

#### 4.3. Production rate

In the process each time the  $\text{Na}^+$  ions cross a cation exchange membrane and enter a compartment, a conversion of methanol to the alkoxide is to be expected. This holds good for the cathode compartment as well as the concentrate compartment. The production rate of the alkoxide may be derived as an average over the total duration of ED and for the total membrane area offered for the crossing of the  $\text{Na}^+$  ions. The rate was of the order of 0.8–3 mol/m<sup>2</sup> h methoxide.

The quantity of the acid produced is of the same order or nearly equal to that of the alkoxide in each run (Table 2); the molar ratio of alkoxide: acid lies in the

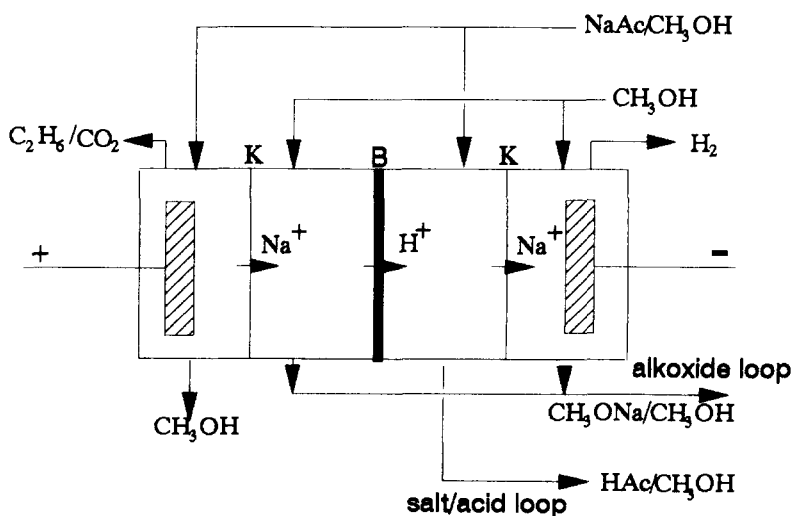


Fig. 2. Simplified electrodialysis cell between the electrode chambers: K, cation exchange membrane; B, bipolar membrane.

range of 0.8 to 1.2. If the Kolbe reaction is assumed, the acetate ions in the anode chamber would be converted to gases. Thus, only the salt or salt/acid compartment could be expected to accumulate the acid produced. But for the alkoxide build-up both the cathode compartment as well as the concentrate compartment were available. For this reason, for each mole of alkoxide produced, only half a mole of the acid is to be expected. However, the fact that roughly equimolar amounts of acid are produced, suggests that the acid is being produced also in the anode compartment. The separation of the anode compartment in run 4 gave proof of this view: for 0.19 mole of alkoxide produced, 0.11 mole of acid was produced in the salt/acid compartment and 0.17 mole in the anode compartment (see Table 2).

Indeed, at these low current densities the Kolbe reaction is not likely to occur at the anode to any significant extent. As also a certain depletion of the acetate ions was to be noted, some other anode reaction involving the consumption of the same as in the Hofer-Moest [3] reaction can be presumed besides an anodic oxidation of the alcohol itself [4]. The protons thus released would form the acid with the acetate ions present. However, it is too early to discuss this aspect at this stage of the investigation, the principal goal of this study being to ascertain whether the production of an alkoxide by way of ED is possible at all.

#### 4.4. Current yield and ion leakage

In general, all other effects being equal, the current yield can be considered to be a measure of the undesirable migration of ions ("leakage") through the membranes. These migrations are illustrated in Fig. 3 (wavy arrows) for a three-compartment cell, which can also be projected for a two-compartment cell (runs 2 to 4). Only in the latter case the migration across the single anion exchange membrane is to be ignored as such a membrane is absent.

The results of the runs can be broadly interpreted with the help of these undesirable ion migrations; however, it must be borne in mind that a rigorous comparison of the runs is not possible, for the conditions (duration, membranes, etc.) were not identical. The difference in current yield between runs 3 and 4 (Table 3) is apparently due to the difference in the nature of the bipolar membranes. A separate systematic

study under identical conditions will be needed to arrive at a final view on the factors leading to a high current yield.

To the extent the acid is dissociated, a corresponding flux of the free protons through the cation exchange membranes is to be expected, with free passage of protons from the acid compartment all the way to the cathode chamber. Likewise, the protons entering or being liberated in the anode compartment would migrate to the alkoxide chamber; here alcohol is being split to form the alkoxide ions. Therefore, the presence of the protons would lead to a recombination with the alkoxide ions to form alcohol instead of the alkoxide, thus reducing the current yield. Virtually, a passage of protons through all the membranes (proton leakage in anion exchange membranes) can be presumed, which could be of significance at high current densities.

The acetate ions are not totally blocked by the cation exchange membrane of the membrane pair or by the bipolar membrane. They do migrate towards the anode and enter the alkoxide compartment reappearing as sodium acetate. They may also further cross the cation exchange membrane and reach the anode compartment.

A quantitative measure of the leakage of the acetate ions would be the total amount in moles of sodium acetate produced in the alkoxide cycle per mole of alkoxide produced. This amounts to the reduction of the alkoxide yield as the acetate ions compete with the alkoxide ions for combination with the sodium ions (a further leakage of the  $\text{Na}^+$  ions to the salt loop is ignored). These values are given in Table 3. The ratios decreased from 1.67 to 0.23 from runs 1 to 2. In other words, the gravity of the leakage of acetate ions was reduced. From run 2 onwards, for lower ratios the current yield for alkoxide attains values over 50%. In the last two short runs of 6 h no appreciable acetate ion leakage into the alkoxide loop was found. Only longer runs make the leakage evident.

The  $\text{Na}^+$  ions will not be totally retained by the bipolar or anion exchange membranes. The ions do migrate towards the cathode, cross the double membrane or the bipolar membrane and reach the acid loop. This leads to a salt formation with the acetate ions of the acid.

A measure of the sodium ion leakage would be the amount in moles of sodium acetate, per mole acid produced, to be found in the acid cycle (run 1). This leakage again amounts to the reduction of the current

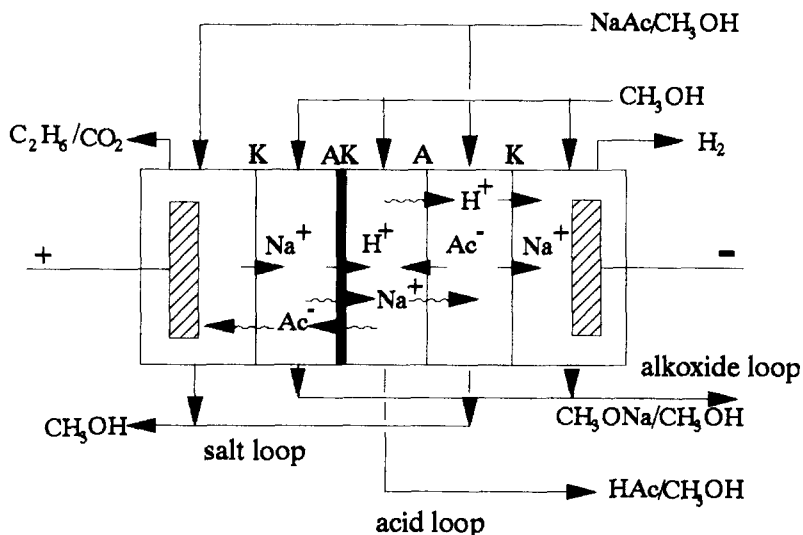


Fig. 3. Ion leakages during electrodialysis: K, cation exchange membrane; A, anion exchange membrane.

Table 3  
Dependence of current yield and ion leakage

Run	Mean current density (A/m <sup>2</sup> )	Duration (h)	Current yield (%)		Ion leakage ratios (mol/mol)	
			NaOCH <sub>3</sub>	Acid	Acetate in alkoxide cycle/ Alkoxide	Acetate in acid cycle/ Acid
1	192	71	10	8	1.67	5.06
2	57	25	55	55	0.23	
3	130	6.0	63	74	0.08	
4	99	5.8	44	40	0	

yield of the acid, as the sodium ions compete with the protons for combination with the acetate ions. The ratio was 5.1. The values for further runs cannot be given as the acid and salt loops were combined and the acetate formed by the entry of Na<sup>+</sup> ions cannot be separately estimated.

## 5. Conclusion

The method of electrodialysis (ED) is usually considered as a desalination process to be applied to saline solutions. The wider scope of this unit operation has been only gradually realized in the recent past. Furthermore, attention has been given only to applications in aqueous media. Accordingly, the membranes and equipment are conventionally made only for desalination of aqueous systems; in our opinion there is no

justification for such a myopic view. For a wide application in chemical processes also ED in non-aqueous media must be given equal attention. One such instance has been considered in this paper.

The purpose of the investigation was to verify whether the production of an alkoxide starting from an alcohol can be carried out by way of ED. The results have shown beyond any doubt that it is possible. In fact, this is just an extension of the known effects of salt splitting and water splitting carried out in aqueous media with the help of mono- and bi-polar membranes, respectively: the ions of a salt MX are separated by way of conventional ED with monopolar membranes and water is split with the help of bipolar membranes in the same stack. This leads to the formation of the corresponding acid HX and base MOH.



In our case a similar double decomposition was carried out with an alcohol as in Eq. (2) or in general,



Thus, in our opinion, the splitting of an alcohol has been shown to be possible for the first time. In which region this takes place and which mechanism is operative are questions demanding further investigation. The models suggested for aqueous media [5] could be of help also here.

## References

- [1] Ullmann Encyclopedia of Industrial Chemistry, Vol. A1, 1995, p. 300.
- [2] C.H. Hamann, German Pat., DE 33 46 131 (1985).
- [3] J. Volke and F. Liska, Electrochemistry in Organic Synthesis, Springer Verlag, 1994, p. 73.
- [4] J. Volke and F. Liska, Electrochemistry in Organic Synthesis, Springer Verlag, 1994, p. 57.
- [5] J. Jörissen and K.H. Simmrock, J. Appl. Electrochem., 21 (1991) 869.

# Electrodialysis in a non-aqueous medium: A clean process for the production of acetoacetic ester

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## Abstract

Alkoxide is used as an agent and consumed in condensation reactions, e.g., in the production of acetoacetic ester. Working in an alcoholic medium and starting from a salt, it is possible to produce an alkoxide by means of electro dialysis. This principle was applied successfully for the production of acetoacetic ester and the recovery of the alkoxide in a single step. Such a process would offer self-sufficiency; the alkoxide could be recovered, thus foregoing the use of mineral acids and the consequent production of a salt as a waste. The merits can be seen in an economical as well as in an ecological context.

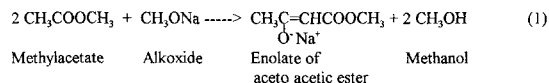
**Keywords:** Electrodialysis; Non-aqueous medium; Alkoxide; Acetoacetic ester; Claisen condensation

## 1. Introduction

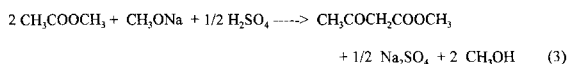
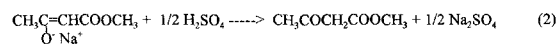
Alkali alkoxides are effective agents in various syntheses such as the Claisen condensation and the intramolecular Dieckmann condensation. They can be best illustrated by the production of acetoacetic ester which itself is a very important starting substance for various further syntheses. Starting with an acetic ester, the synthesis is carried out in two steps in conventional reactors [1,2]. The first step of condensation employing an alkoxide produces the acetoacetic ester in its enolate form. The free ester can then be recovered from the enolate by a further

reaction with an acid, e.g., sulphuric acid; this step is called protonation.

### (1) Condensation



### (2) Protonation



Such a synthesis involves the consumption of the valuable alkoxide in quantities equivalent to the product. Furthermore, equivalent quantities of an

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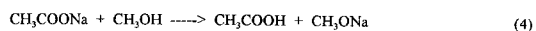


extraneous acid must be employed [sum Eq. (3)]. Also the production of superfluous methanol as well as sodium sulphate (pollution) must be borne in mind.

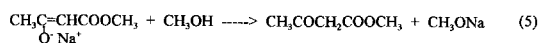
At present, the technical production of the acetoacetic ester relies on the production of ketene and diketene as intermediate products formed by dehydration of acetic acid. Both the compounds are toxic and hazardous [3]. Ketene is an extremely toxic gas ranking with phosgene; diketene is a flammable liquid and must be stored cold and under nitrogen. Otherwise, it is given to exothermic polymerisation which could lead to explosions. Yet, such a route is preferred although the route of Claisen condensation offers a simple and harmless alternative. The reason is probably the consumption of the alkoxide in the latter case which makes the process uneconomical. Furthermore, the salt production would also make the process environmentally prohibitive. The method described here offers an improvement of the synthesis based on the safe Claisen condensation and stands out as an alternative to the hazardous ketene/diketene route.

## 2. Principle of the electrodialytic method with bipolar membranes

In a previous paper [4], a similar method was described to produce an alkoxide starting from an alkali salt employing the method of electrodialysis with bipolar membranes. Working in methanoic solutions and starting with a salt as the source for sodium, the corresponding acid and the sodium alkoxide could be produced with the sum equation:



This finding offers not only a new method of production of the alkoxide: if the sodium enolate of the acetoacetic ester produced by condensation is to be used as the sodium source in lieu of the acetate, Eq. (4) can be re-written as

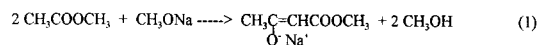


with the formation of the free ester. In this step

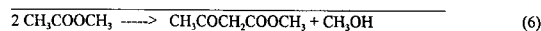
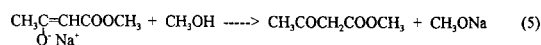
methanol replaces the sulphuric acid for protonation [cf. Eq. (2)].

Basically, the Eqs. (1) and (5) would form the principle of such a new process:

### (1) Condensation



### (2) protonation:



The protonation would be carried out with the very alcohol that is being produced in condensation, the latter serving as the 'acid'. The amount of methanol formed is thus reduced by half [cf. Eq. (6) with Eq. (3)]. No salt would be formed.

## 3. Experimental

The electrodialysis stack (see Fig. 1 and cf. [4]) consisted of the electrodes, two cation exchange membranes (cem) and a bipolar membrane (bpm). The sodium enolate was introduced here into the diluate chamber as a methanoic solution for protona-

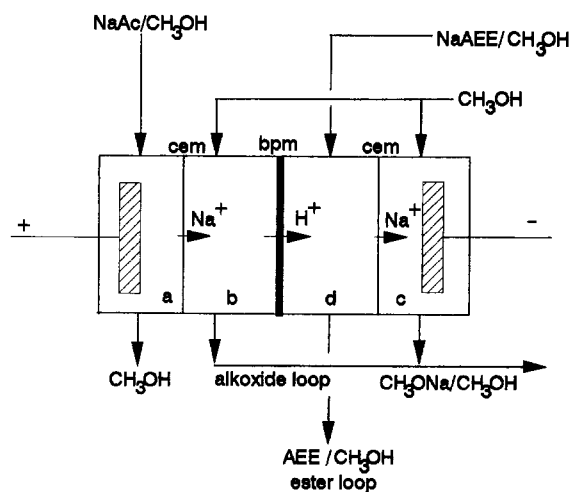


Fig. 1. Protonation to produce acetoacetic ester. Abbreviations: cem: cation exchange membrane, bpm: bipolar membrane, NaAc: sodium acetate, AEE: acetoacetic ester, NaAEE: enolate of acetoacetic ester.

tion. The experiments [5] were conducted starting with the following solutions:

- Anolyte: 12 wt% sodium acetate in methanol, 1.2–1.5 kg.  
 Concentrate: Methanol with 1.2 wt% sodium methoxide (added to ensure conductivity at the beginning of the run), 1.4–1.45 kg.  
 Diluate: 8.5–9.6 wt% sodium enolate of acetoacetic ester in methanol, 1.2–1.6 kg.  
 Catholyte: The same solution as concentrate, 1.2–1.43 kg.

The enolate was furnished by the company Fluka and had a purity of > 95%. The alkoxide (> 99% pure) was of Hüls AG.

The temperature was maintained at 20 to 22°C by cooling each circuit with the help of thermostats. The current densities were varied from one run to the other (Table 1). In runs 1, 4 and 5, a constant current strength was maintained by constantly increasing the voltage from about 20 to 80 V towards the end. In runs 2 and 3, a constant voltage of 40 V was applied with the current strength dropping with time. The specific conductivities of the streams which were measured on-line were in the range of 1 to 20 mS/cm.

Various analytical methods were applied to samples taken from the solutions. The methods included elementary analysis, potentiometry and gas chromatography [5].

## 4. Results and discussion

### 4.1. The production of alkoxide

The alkoxide is produced from two different sources: on the one hand, in the concentrate compart-

ment b with the sodium acetate in the anolyte as the source for the sodium ions. On the other hand, also the enolate in the diluate compartment d contributes to sodium ions leading to alkoxide formation in the catholyte compartment c. These individual contributions which were of the same order, have been summed up and given in Table 1 as the total production of alkoxide. The effectiveness of the formation of alkoxide by the sodium ions released by the protonation of the enolate can be assessed by the selectivity:

$$s_{\text{Alk}} = \frac{\text{moles of alkoxide produced in the catholyte}}{\text{moles of Na-enolate consumed}} \quad (7)$$

The values for the enolate consumed and alkoxide produced match well (cf. Table 2) with the selectivity at > 90%, showing the reappearance of almost all of the sodium as alkoxide. No other sodium compounds were found in the catholyte. The current yield was in the range of 70–75%.

### 4.2. The production of acetoacetic ester

The ester is produced in the diluate loop by the protonation of the enolate. A measure of the amount of free ester being formed from the enolate is the selectivity

$$s_{\text{AEE}} = \frac{\text{moles of ester formed in the diluate}}{\text{moles of enolate disappearing in the diluate}} \quad (8)$$

The values (Table 3) are not as high as in the case of the alkoxide, indicating the fact that the enolate being protonated is not yielding only the free ester. However, further work is needed to identify all the other compounds being formed. Also, the experimental conditions hitherto chosen arbitrarily must be

Table 1  
Enolate consumption and production of alkoxide

Run	Duration density (h)	Current of enolate (mA/cm <sup>2</sup> )	Consumption produced		Total alkoxide (mol)
			(mol)	(%)	
1	24	4.9	0.40	38.0	0.62
2	24	8.8 <sup>a</sup>	0.587	58.7	1.12
3	24	13.8 <sup>a</sup>	0.865	96.6	1.76
4	25.5	9.9	0.77	92.2	1.29
5	43.25	6.0	0.76	93.8	1.41

<sup>a</sup> Mean values.

Table 2  
The production of alkoxide

Run	Alkoxide produced in concentrate (mol)	Alkoxide produced in catholyte (mol)	Selectivity, $s_{\text{Alk}}$ (%)	Current yield, $\zeta$ (%)
1	0.26	0.36	90.0	70.7
2	0.56	0.56	95.4	71.2
3	0.86	0.90	100	72.5
4	0.58	0.71	92.2	72.5
5	0.67	0.74	97.4	75.2

altered in order to maximize the selectivity and the current yield for the ester.

#### 4.3. Simultaneous condensation and protonation in the electrodialysis stack

Instead of recovering the alkoxide in the electrodialysis step and returning it to a prior condensation step, one can think of carrying out the condensation in the concentration chamber itself. Here the alkoxide produced by the reaction of the  $\text{Na}^+$ -ions with the methanol solvent can be used up in situ to form the enolate of acetoacetic ester from the acetic ester [Eq. (1)]. After attaining a chosen degree of conversion, the concentrate containing the enolate is fed to the adjacent diluate chamber for protonation (Fig. 2). The anolyte can be any sodium source such as sodium acetate as shown in the figure or sodium methoxide as in the run described below. The catholyte *c* and diluate *d* are the same as in the case already discussed (cf. Fig. 1). In case the condensation reaction turns out to be the limiting step, the concentrate chamber could be passed through an external heated reactor to accelerate the condensation and then cooled before its return to the stack.

A trial run was made at room temperature and under the same electrical conditions as in the previ-

Table 3  
The production of acetoacetic ester

Run	Acetoacetic ester produced in diluate (mol)	Selectivity, $s_{\text{AEE}}$ (%)	Current yield, $\zeta$ (%)
1	0.15	37.5	34.5
2	0.38	64.7	48.3
3	0.57	65.9	46.1
4	0.35	45.5	35.3
5	0.49	64.5	50.6

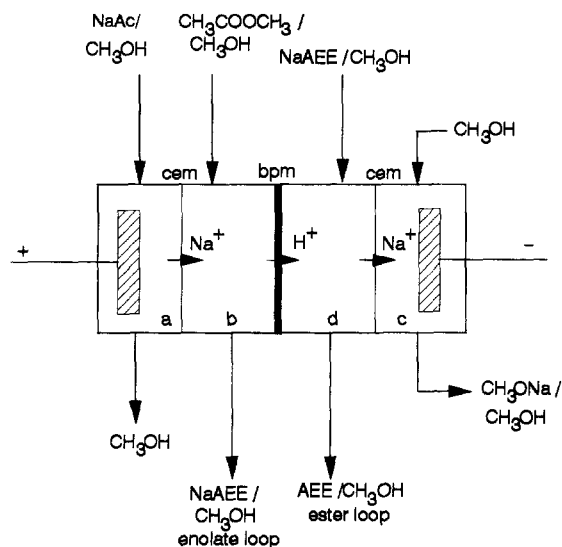


Fig. 2. Condensation and protonation in a single step. Abbreviations: see Fig. 1.

ous runs but with the concentrate chamber at 50°C. The solutions employed were:

Anolyte: 5.7 wt% sodium methoxide in methanol.

Concentrate: 70 wt% methyl acetate + 29.0 wt% methanol with 1 wt% sodium methoxide (added to ensure conductivity at the beginning of the run).

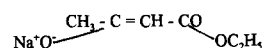
Diluate: as in the previous runs.

Catholyte: 1.2 wt% sodium methoxide in methanol.

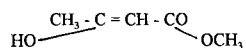
The circuits were kept separate during the whole run of 22.6 h. 19.2 g (0.14 mol) of the sodium salt of the ester (i.e., acetoacetic ester in the enolate form) were produced in the concentrate chamber, with a corresponding protonation in the diluate chamber. This initial run must be followed by further runs under improved conditions as the current yield for the ester was only of the order of 23%.

#### 4.4. Transesterification

An interesting observation was made in one of the initial runs: in this run the enolate employed was the *ethyl* derivative of the acetoacetic ester:



dissolved in methanol. The solution had a concentration of 7.5 wt% ester. The electrodialysis proceeded at room temperature and for 28 h. The analysis was carried out along the same lines as already described in Section 3. On analysis of the diluate it was found that along with the protonation also a transesterification had taken place yielding the *methyl* derivative (given below in the enolic form)



97% of the free ester found was the methyl ester, with only 3% ethyl ester. The enolate had been attacked at both ends by the methanol, viz. at the enolic group (protonation) and at the carbonic acid group of the enolate (transesterification) as well.

A methanolic solution of the ethyl ester of the same molar concentrate as of the enolate in the previous electrodialysis run, was placed in two glass vessels and stirred under identical conditions and for the same duration as in the run. In one of the vessels, samples of the cation exchange as well as bipolar membranes were also placed, with the same ratio of the membrane area to the sample volume as in the electrodialysis run. The membranes had been conditioned as in the case of the various runs (Section 3). Only the electrical field was absent. Also here a transesterification took place but the conversion was only in the range of 25–30%. According to these results the protonation in an electrical field appears to play a significant role in the transesterification process.

## 5. Conclusion

The preliminary results presented here show that a process based on the principle of alkoxide recovery by way of protonation is fundamentally feasible. It must be borne in mind that the optimal conditions for the process have yet to be found. Moreover, also sufficient improvement can be expected by choice or development of the membranes for such non-aqueous media.

However, even at this stage the following merits of the process may be mentioned as the highlights:

(1) The process becomes self-sufficient with respect to the alkoxide. This would give the process a major cost advantage.

(2) The production of methanol is reduced by half (cf. Section 2), with the amount having its source in the alkoxide being retained in the system. Only the part originating from the ester used for acetylation has to be removed.

(3) There is no need to use an extraneous acid like sulphuric acid for protonation.

(4) Both the steps of condensation and protonation could be even carried out in a single step of electrodialysis, with the alkoxide produced being immediately consumed to produce the enolate in the same chamber (cf. Section 4.3).

(5) The introduction of sodium in the form of valuable alkoxide in equivalent amounts, and its discharge as a worthless salt is avoided. Sodium is recycled and maintained within the system. This amounts to a clean production with an economical and an important ecological merit.

Along these lines, also new possibilities for other conventional reactions could be envisaged making them economically and ecologically attractive.

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## References

- [1] DRP 526691, 1928 to Wacker.
- [2] DRP 558469, 1931 to Wacker.
- [3] Kirk-Othmer, Ketenes and related substances, *Encycl. Chem. Technol.*, 13 (1978) 874.
- [4] S. Sridhar, Electrodialysis in a non-aqueous medium: production of sodium ethoxide, *J. Membrane Sci.*, 113 (1996) 73.
- [5] C. Feldmann, Elektrodialytische Herstellung von Acetessigester unter Verwendung bipolarer Membranen, Thesis work: Diplomarbeit, Fachbereich Chemieingenieurwesen, Abteilung Steinfurt, Fachhochschule Münster, 1994.