

Electrosynthesis of adiponitrile in undivided cells

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It has been shown that adiponitrile can be synthesized in undivided cells under favourable conditions. Because of strong decomposition of the quaternary ammonium salt support electrolyte, its concentration must be kept at a very low level. To avoid excessive resistance of the cell, the distance between the electrodes must then be smaller than 0.5 mm. We have developed various types of such cells. The 'capillary gap cell' is simple in design and can be readily scaled up. Continuous operation is possible. Yields of about 90% of adiponitrile have been obtained. The energy consumption is less than 3 kWh/kg product. Work up of the solutions is greatly facilitated by the low salt concentrations. It has been shown that the anodic oxidation of isopropanol, which is used as cosolvent, is strongly influenced by the acrylonitrile present. A substantial portion of the isopropanol is oxidized to CO₂.

1. Introduction

Some ten years ago M. Baizer of Monsanto showed that adiponitrile could be synthesized via acrylonitrile by a direct electrochemical reaction. His new process for the manufacture of an important intermediate for Nylon 66, starting from an inexpensive raw material and giving the desired product in good yield, has found wide interest.

Baizer's pioneer work has given a strong impetus to the industrial development of organic electrochemistry. Research in this field has also increased substantially in the succeeding years. Monsanto [1] and other companies [2] have described the application of divided cells using ion exchange membranes as diaphragms for this synthesis. From a technical point of view, the application of undivided cells would be highly desirable as the construction of such industrial cells is relatively simple. Many problems which are involved in the use of diaphragms are avoided; for instance, the lack of mechanical endurance, swelling or erosion by the solvent, sealing of the electrode compartments, electro-osmosis of water, high ohmic resistance, forma-

tion of hot spots and the necessity of providing two separate electrolyte loops. The low electrolytic conductivities, which are typical of organic systems, make it necessary to minimize the distance between the electrodes. This aim can be realized more effectively and more simply if diaphragms are avoided.

The question 'with or without diaphragm' is of fundamental importance for any type of electrolysis. A diaphragm cannot be dispensed with if the electrode process is reversed at the counter electrode or if the starting material or the product is electrochemically attacked at the counter electrode in some other way. In the case of acrylonitrile, the cathodic reaction is irreversible and, moreover, acrylonitrile is fairly stable at the anode; this also holds for other nitriles. It is therefore not surprising that there should be numerous publications dealing with the cathodic reactions of acrylonitrile, but there is practically no literature on anodic reactions. In two papers, the anodic formation in low yields of a product of free radical polymerization is reported [3, 4]. The basic conditions for a successful electrosynthesis in undivided cells therefore looked favourable.

2. Investigations at High Salt Concentrations

We began by electrolyzing in undivided cells the reaction mixtures proposed by Baizer [1] which contain high concentrations of lyotropic quaternary ammonium salts. Some typical preparative results are shown in Table 1 for experiments using platinum sheet as the anode. It can be seen that the yield of adiponitrile is at least 7% lower than in comparable runs carried out with divided cells and that the current efficiency is also lower. More by-products are generated, which are distillable (S) as well as non-distillable (R). Baizer has reported a yield of 80% in electrolyzing the system at the top of Table 1 in an undivided cell [5], which agrees with our results. Optimum results are obtained by reducing the salt concentration to 12% and additionally introducing acetonitrile as a cosolvent.

During electrolysis the electrolyte turns brown to black. The pH decreases so that a base must be added to keep it at the desired level of 9.5. We have found by a titrimetric method that in the case of tetraethylammonium-p-toluenesulphonate, two acid compounds are formed with pK values of 4.8 and 10.1, the quantities being proportional to the electrolysis time (Fig. 1). These results can be explained as follows: The methyl group of the tosylate anion is anodically oxidized to the carboxyl group. In addition, phenolic OH groups are introduced into the ring. These processes take place with current efficiencies, β , of 36 and 12%, while the evolution of oxygen is found to

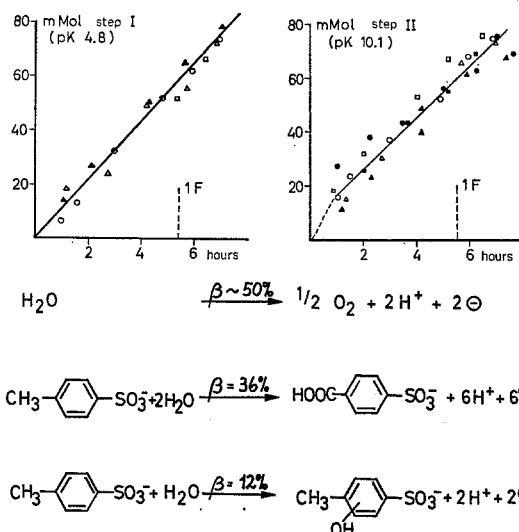


Fig. 1. Anodic formation of acid products (Pt, pH 3.5, 35% NEt₄-tosylate, 40% AN, $j = 10 \text{ A/dm}^2$, $i = 5 \text{ A}$).

proceed with a current efficiency of about 50%. Similar results are obtained with other lyotropic quaternary ammonium salts at Pt, graphite and lead dioxide anodes. The anodic oxidation of p-toluenesulphonic acid has been reported elsewhere [6].

These results show that the quaternary ammonium salt is markedly attacked at the anode and electrolysis under these conditions would not therefore be economical. Moreover, the product would not be obtained in the desired purity. Electrolyses in undivided cells could alternatively be carried out using the electrolytes proposed by Rhône-Poulenc, namely, quaternary ammonium salts with stable anions such as

Table 1. Electrolysis of acrylonitrile in divided and undivided cells.

Cathode: amalgamated Pb(3)Hg(1), $j = 10 \text{ A/dm}^2$, pH = 9.5, 40% AN, $x\%$ Salt $y\%$ Solvent, $(60 - x - y)\%$ Water, Conversion 50%, Anode: Pt.

X (%)	Quaternary ammonium salt	Y (%)	Solvent	Diaphragm (sintered Alundum cup)	Yield (%)				Current efficiency (ADN) (%)
					ADN	PN	S	R	
34	NEt ₄ PTS	—	—	+	89.0	1.0	2.0	8.0	90
34	NEt ₄ PTS	—	—	—	80.5	1.1	4.0	14.4	82
34	NEt ₄ EtSO ₄	—	—	+	87.0	0.8	6.3	5.9	95.5
34	NEt ₄ EtSO ₄	—	—	—	80.3	1.4	7.0	11.3	84
30	NEt ₄ CF ₃ COO	—	—	+	85.5	1.0	3.2	10.3	82
30	NEt ₄ CF ₃ COO	—	—	—	78.2	1.0	10.2	10.6	83
12	NEt ₄ PTS	28	Dioxane	+	87.0	1.1	4.6	7.3	87
12	NEt ₄ PTS	28	Dioxane	—	74.2	5.5	10.2	10.1	70
12	NEt ₄ PTS	33	Acetonitrile	+	92.8	1.0	1.0	5.2	89
12	NEt ₄ PTS	33	Acetonitrile	—	86.2	1.3	6.1	6.4	68

sulphate or phosphate [7]. The use of alkali metal salts alone is not possible, as the cations have to build up a hydrophobic layer at the surface of the cathode to avoid excessive formation of propionitrile [8]. Tomilow *et al.* have shown, however, [9] that the addition of small amounts of quaternary ammonium salts to an aqueous alkali metal phosphate buffer will give excellent results using emulsified acrylonitrile. The process has been improved recently by the introduction of polyphosphates [10].

A further possibility is the use of special anodes having a low overvoltage for the anodic evolution of oxygen. We have done some work in this direction the results of which are shown in Table 2. The corrosion of the anodes (area about 10 cm²) was found by weighing after the passage of 5–10 Ah. The average anode potential \bar{E}_A is given with respect to a saturated calomel electrode; the extinction of the solution after the test is a measure of the discolouration.

The first groups of anodes in Table 2 consists of precious metals and their alloys. Corrosion was appreciable in all cases, even with platinum, which corroded at the rate of about 1 mg per Ah. This high value has been ascribed to the influence of the acrylonitrile [9]. The potentials were high and the solutions were discoloured after the tests, as shown by the extinctions. On the other hand nickel and its alloys gave less positive potentials and negligible discolouration; the current efficiency for oxygen was high in some cases. However, none of the anodes was sufficiently passivated and the rates of corrosion were therefore high. Alloying with platinum lowered the corrosion rate appreciably, but the potential became so positive that the decomposition of the quaternary ammonium salt was similar to that at pure platinum. Fig. 2 shows the corresponding current voltage curves. In the presence of platinum the Tafel lines are rather flat. Some alloys of Mo and Ta which are usually

Table 2. Corrosion of anodes.

In 40% AN/34% NEt₄PTS/26% H₂O at 35°C and 10 A/dm². Cathode: amalgamated lead—conversion of acrylonitrile < 50%

Anode	Anodic corrosion [mg/Ah]	\bar{E}_A [V]	O ₂ -Current efficiency (%) ± 5%	Discolouration E _{300mμ}
Pt	1.0	2.80	50	0.200
Pt, platinized	—	2.20	30	0.090
Pt (90) Ir (10)	0.8	2.83	30	0.234
Pd	6.9	1.8–3.3	80	0.004
Pd (50) Pt (50)	4.5	2.57	60	0.148
Au	34	2.04	50	0.041
Au (50) Pt (50)	3.3	2.77	35	0.172
Au (90) Pt (10)	30	2.20	40	—
Pt (50) Ni (50)	4.5	2.18	75	0.106
Pt (65) Ni (35)	3.2	2.57	60	0.148
Ni	146	1.85	75	0.023
Ni (95) Si (5)	190	1.86	80	0.008
Ni (90) Si (10)	158	2.26	85	0.007
Ni (95) Ge (5)	119	1.83	90	0.020
Ni (90) Sn (10)	104	1.88	85	0.033
Ni (90) Pb (10)	192	1.64	70	0.012
Ni (96) B (4)	374	1.74	60	0.008
Fe (90) Si (10)	120	1.74	40	—
Mo (60) Ru (40)	220	4.1		
Mo (60) Pd (40)	190	5.8		
Mo (70) Os (30)	200	4.0		
Ta (60) Ru (40)	380	1.9		
Ta (69) Os (31)	13.5	6.0		
Mo (85) Re (15)	320	8.0		

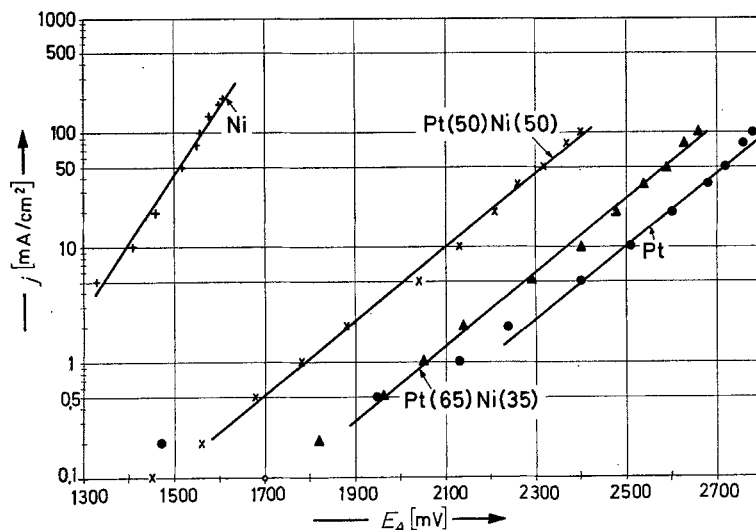


Fig. 2. Anodic current-potential curves at Ni, Pt and their alloys (40% AN, 34% $\text{NEt}_4\text{-p-toluenesulphonate}$, 26% H_2O , pH 9, 35°C).

very resistant against corrosion, also show high corrosion rates under these conditions.*

3. Investigations at Low Salt Concentrations

3.1. Introductory remarks

The rather discouraging results obtained at high salt concentrations led us to conclude that it would be advantageous to work at the lowest possible salt concentration and we have consistently pursued this line of thought. In order to be able to carry out electrolyses at technical current densities in electrolytes having the expected low conductivities, cells with an extremely small distance between the electrodes are required. Fig. 3 summarizes the results of our development. The first two cells have liquid-permeable electrode pairs (stationary or vibrating), while the other two have non-permeable electrodes. In the former case, the solution flows perpendicularly through the electrodes; in the latter parallel to the electrodes in a capillary gap. Such a capillary gap is also formed when the anode dips into the mercury cathode and the solutions flows against the submerged anode surface. In all the examples, the distance between the electrodes is as small as a few tenths of a milli-

* We wish to thank Dr G. Böhn of BASF's Materials Testing Laboratory for making these alloys available to us.

Type	Cell	Cathode/ Anode	*Cell voltage [V] at current density [A/dm ²]		
			10	20	50
Liquid permeable electrodes		lead/ lead dioxide	5.9	7.3	—
		lead/ lead dioxide	5.3	6.5	10.0
Nonpermeable electrodes		carbon/ lead dioxide	4.5	5.3	—
		mercury/ lead dioxide	5.5	6.5	9.0

Fig. 3. Undivided cell with minimized distance between electrodes.

* Concentration of $\text{NEt}_4\text{EtSO}_4$ in the first three cells: 0.5%; in the last cell: 1.0%

metre. The voltages at various current densities show clearly that these cells allow the electrolysis to be conducted at industrial current densities in spite of the low salt concentration. This value (0.5%) is lower by a factor of 68 than the high concentrations previously used, which leads to a lowering of the specific conductivity

by a factor of 15 (from 20 to 1.3 mho/cm). This effect seems to be overcompensated by the lowering of the electrode distance, for the voltage is more favourable at any given current density. Our work on the development of these new cells is described elsewhere [11], therefore we shall discuss here in detail only the capillary gap cell, which appears to give the lowest voltages in this system.

3.2. Capillary gap cell

(a) *Theory* [11]. A capillary gap is formed by two rectangular, parallel plates of length l , width b and distance d . A liquid of specific gravity ρ and specific viscosity η is forced to flow in the capillary gap by a pressure difference Δp existing between the ends of the gap. The rate of capillary flow is determined by the equation

$$\dot{m}_k = \frac{\rho}{6\eta} \cdot \Delta p \cdot \frac{a}{l} d^3 \quad (1)$$

The Faradaic conversion of substrate passing through the gap becomes quantitative at the following flow rate:

$$\dot{m}_s = \alpha \cdot F \cdot \kappa \cdot \frac{\Delta E}{c} \cdot a l \frac{1}{d} \quad (2)$$

α = current efficiency

F = electrochemical equivalent

κ = specific conductivity

ΔE = voltage drop in electrolyte

c = concentration of substrate.

Regarding the removal of Joule's heat, the flow rate which must be reached in order not to exceed a permissible increase in temperature $\Delta\theta$, is calculated from

$$\dot{m}_w = \frac{\kappa}{h} \cdot \frac{\Delta E^2}{\Delta\theta} \cdot a l \frac{1}{d} \quad (3)$$

(h = specific heat of electrolyte)

These three equations are plotted in Fig. 4 using practical parameters for the electrolysis of acrylonitrile ($c = 50\%$, $\kappa = 10^{-3}$ mho/cm, $\Delta E = 1V$). The intersection between the curve for capillary flow (1) and the curves for consumption of substrate (2) and heat generation (3) gives the lower limit for the distance between the electrodes. It can be seen that this limit is about 0.1

mm. It increases as the length and width of the capillary gap are increased.

(b) *Design of the cell*. Fig. 5 shows one of the possible designs of the capillary gap cell [12]. It is made up of a stack of circular round horizontal disks (1). Exact planarity is easier to obtain with circular disks than with rectangular plates. The capillary gap (2) of 0.2 mm thickness is maintained by radially arranged strips of polyester material. The electrolyte flows radially outward from the centre (3) of the stack. It is recycled

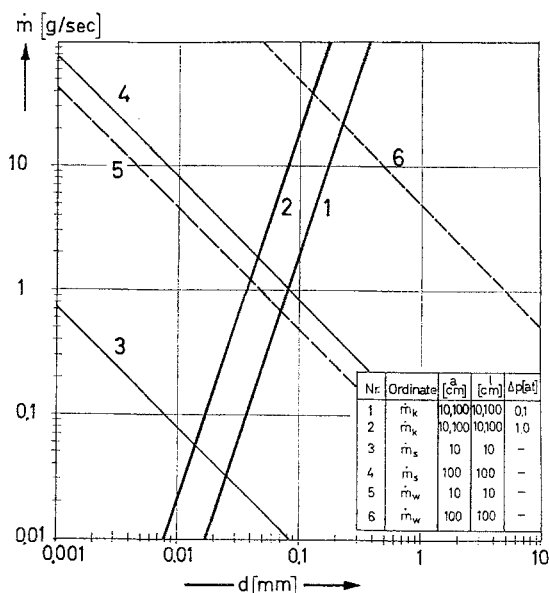


Fig. 4. Rate of flow versus distance of electrodes.

through a heat exchanger (4). The stack may be submerged in the electrolyte. If it is not submerged, capillary forces keep the gaps filled with liquid and the filling volume is then also very small. The plates are connected in series in a bipolar manner and (5) and (6) serve as the current leads. The disks as well as the cathodes consist of graphite while the anode is a thin layer of lead dioxide which can be deposited electrolytically. Isolation of the electrode pairs at the rims is not necessary as the distance between the electrodes is about one hundredth of the distance between the electrode pairs. Stray currents can therefore be neglected. Furthermore stray current flowing to more distant parts of the system can be disregarded as the conductivity of the solution is very low. Continuous operation

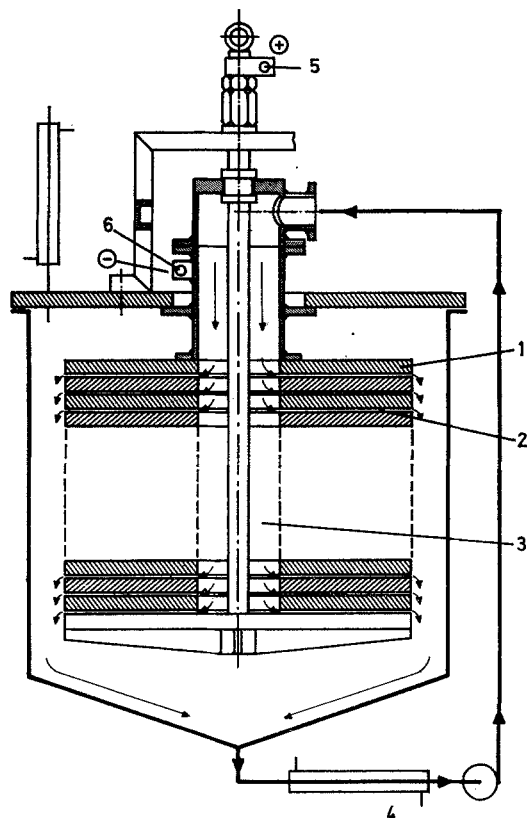


Fig. 5. Design of capillary gap cell (circular disks (1) of inert, conducting material, (2) capillary gap, (3) centre of the stack, (4) heat exchanger, (5), (6) current leads.

offers no problem. The cell is basically a loop. It must therefore be fitted with an inlet for make-up of the reaction mixture and an outlet for partly reacted mixture.

(c) *Scale up.* Scale up of the cell is achieved by either enlarging the area of the disks or increasing their number (Fig. 6). The former alternative is limited by the planarity obtainable and the growing residence time of the solution in the gap. A diameter of 50 cm is technically feasible. The latter alternative is limited by the maximum voltage of industrial power sources and by the increase in stray currents at high voltages. Up to about 100 disks are possible however giving a total stack voltage of 400–500 volts. Several stacks can be arranged in the same case to form a cell block. The stacks are arranged in parallel with reference to both circulating solution and electric current. Within a stack, the disks are, as

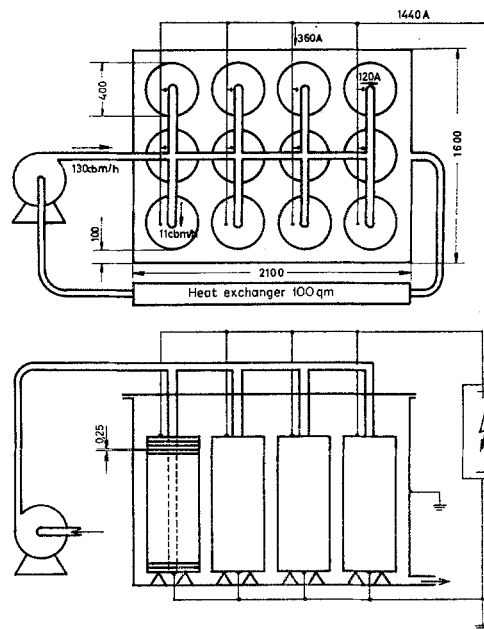


Fig. 6. Electrosynthesis of ADN in the capillary gap cell. Plan and side elevation of a cell block with 12 cell stacks, each containing 100 disks. Capacity 140 tons per month ADN.

already mentioned, connected electrically in series and with reference to the liquid flow in parallel. In the figure, a unit with 12 stacks, each stack consisting of 100 disks with a diameter of 40 cm, is illustrated. Such a cell block can produce 140 tons of adiponitrile in a month, in spite of the low current density of only 10 A/dm^2 . The space-time yield is $0.05/\text{h}$ with reference to the volume of the cell block, but about $7/\text{h}$ with reference to the volume of the electrolyte in the gap between the electrodes.

(d) *Work up.* The low concentration of quaternary ammonium salt greatly facilitates the working up of the discharge. According to Fig. 7, a mixture of acrylonitrile (AN), isopropanol (IP, as a cosolvent), water and 0.5% quaternary ammonium salt (Q) is reacted in the cell up to a conversion of 60% based on acrylonitrile, whose stationary concentration will be about 20%. The product level is about 30%. The low boiling components in the effluent from the cell are stripped in an evaporator and separated in column K_0 . Separation of acetone need not be quantitative. The small amount of salt and its decomposition products can be eliminated by

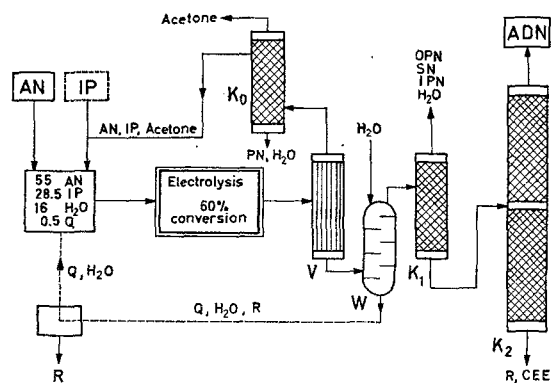


Fig. 7. Continuous working up at low salt concentrations.

washing with water and the recoverable portion is recycled. However, the process is also economical when this step is omitted. In column K_1 , some by-products with intermediate boiling points such as oxypropionitrile (OPN) or succinonitrile (SN) are taken off overhead at reduced pressure. The main product adiponitrile is distilled in the last column at reduced pressure. Non-distillable components include oligomeric acrylonitrile (R). Biscyanoethyl ether (CEE) is also found in the distillation residue.

In spite of electrolysis in an undivided cell a very pure product is obtained which can be hydrogenated to polyamide-grade hexamethylene diamine.

3.3. Results of preparative electrolyses

Results of preparative electrolyses on a laboratory scale will now be discussed. The runs were made batchwise in a cell with six circular disks, each disk having an area of 1 dm^2 . The standard composition of the electrolyte, which was recycled through the cell, was as follows (in per cent by weight): 55% acrylonitrile, 28.5% isopropanol, 16% water and 0.5% tetraethylammoniummethyl sulphate.

Unless otherwise specified the current density was 10 A/dm^2 , the temperature 30°C , the conversion of acrylonitrile 60%, the pH was 3.5 (no base added) and the distance between the electrodes was $125 \mu\text{m}$. The cathode was graphite (Diabon, a product of Sigri AG, Meitingen), the anode a thin layer of lead dioxide. After electrolysis, the solution was clear and had a pale

yellow colour. Analysis of low and high boiling fractions was made by vapour phase chromatography. The proportion of salt in the non-distillable residue was calculated with the aid of elementary analysis for sulphur and nitrogen.

Fig. 8 shows the influence of pH, current density, temperature and electrode distance on the yield of adiponitrile. No appreciable change in yield was observed when changing these parameters. These findings are rather surprising as far as the pH is concerned, for in a divided cell a strong decrease in yield was found at lower pH values [1]. With our cell, no addition of base is therefore necessary to maintain the pH at a high level. The enhancement of the voltage drop is proportional to the distance between the electrodes, namely 6 V/mm which agrees well with the calculated value. On the other hand, a distinct dependence of the yield on the concentration of acrylonitrile has been found (Fig. 9). The second cosolvent used was acetonitrile, whose concentration together with the concentration of acrylonitrile always added up to 55%. The acrylonitrile conversion ranged from 30 to 75%. Optimum yields of about 90% are obtained when starting with a concentration of acrylonitrile of 25%. This is due to the decrease in the amount of polymers formed. A further decrease in AN concentration leads to a strong increase in the amount of propionitrile. According to Fig. 10 similar results are obtained, if acetonitrile is replaced as a second cosolvent by adiponitrile or propionitrile. The favourable result in the case of adiponitrile is important in continuous operation. Methanol is unsuitable as a cosolvent, as it reacts with acrylonitrile to form the product of cyanoethylation [13]. Therefore the yield decreases strongly. The current efficiency also decreases because of the enhanced formation of propionitrile; addition of water does not result in any distinct changes. Even at the highest water concentration the current efficiency remains high.

Table 3 gives the yield of adiponitrile and various by-products for various cathode materials. With carbon, including carbon-filled polymers, lead, and amalgamated copper, similar results are obtained. An exception is copper, where appreciable amounts of propionitrile are formed. Further runs were made with various concentrations of quaternary ammonium salt.

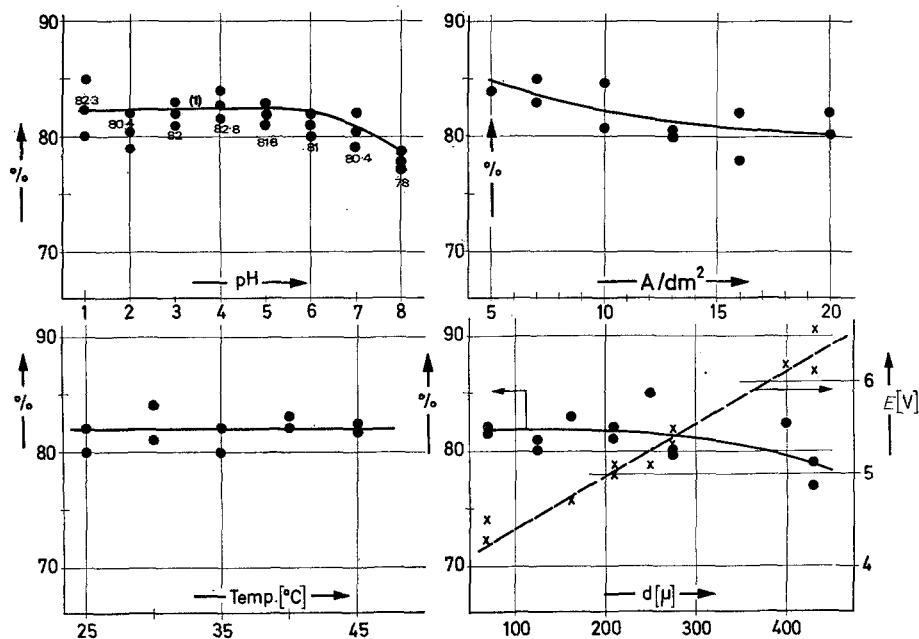


Fig. 8 Yield for adiponitrile as a function of pH-value, current density, temperature and distance of electrodes. (Standards: $d = 0.2$ mm; 55% AN, 28.5% IP, 16% H_2O , 0.5% NBt_4ETSO_4 ; 10 A/dm², pH 3.5, 30°C, 30% conv.)

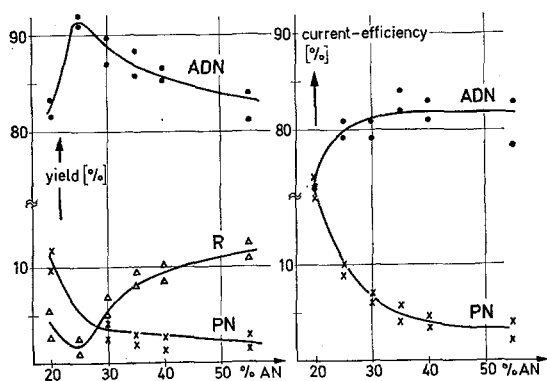


Fig. 9. Influence of AN-concentration (second cosolvent: acetonitrile).

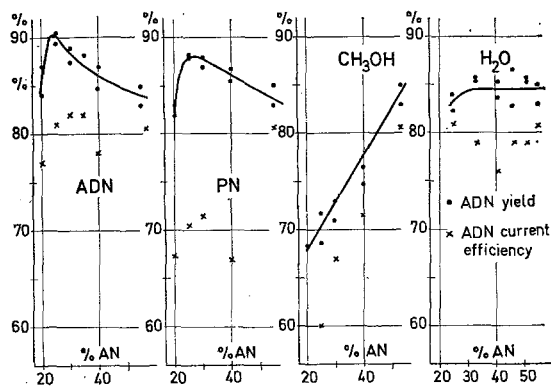


Fig. 10. Influence of AN-concentration \times (with various cosolvents).

According to Table 4, no change in ADN yield is found at salt concentrations between 1.0 and 0.1%. It is only at even smaller concentrations that the formation of propionitrile will increase. From these results it may be concluded that McKee systems have no specific influence on the cathodic hydrodimerization of acrylonitrile.

3.4. Anodic processes

It is important to have sufficient information on

the nature of the anodic processes, because they can influence the cathodic reactions as well as change the purity of the product. We have already shown that at high concentrations of quaternary ammonium salt the salt is strongly attacked at the anode. According to Fig. 11a, the current potential curve with a Pt anode is shifted to a strongly positive potential in the presence of acrylonitrile. Even very small concentrations of acrylonitrile produce a distinct effect in this direction, as may be seen from Fig. 12. This curve

Table 3. Electrolysis of AN at various cathodes.
55% AN, 28.5% IP, 16% H₂O, 0.5% NEt₄EtSO₄
pH 3.5, 30% Conversion, 7A/dm², 30°C

Cathode	Yield (%)				Current efficiency (%)	
	ADN	PN	S	R	ADN	PN
Carbon (Diabon N*)	81.0	0.4	3.6	15.0	82	1
Carbon (EXN†)	80.3	2.4	4.0	13.3	78	5
Graphite-filled phenol-formaldehyde resin (Bascodur‡)	83.6	1.3	2.6	12.5	76	2
Lead	83.4	2.4	4.0	10.2	77	5
Lead, amalgamated	81.0	2.4	4.0	12.6	82	5
Copper	70.9	14.6	3.9	10.6	53	22
Copper, amalgamated	80.1	9.8	4.3	5.8	64	16

* Sigr, Meitingen.

† Conradt, Nürnberg.

‡ Raschig, Ludwigshafen.

Table 4. Electrolysis of AN at low salt concentrations.
55% Acrylonitrile, (29-x)% Isopropanol, 16% H₂O, x%
NEt₄EtSO₄ pH 3.5, 30% conversion, 7A/dm², 30°C

X(%) NEt ₄ EtSO ₄	Yield (%) ADN	Current efficiency (%) ADN	E[V]
1.00	80	81	3.9
0.75	82	83	4.1
0.50	83	81	4.3
0.25	84	84	4.8
0.10	81	80	5.8

was obtained by keeping the current density constant and measuring the stationary anode potential after the addition of acrylonitrile. Similar results are obtained by investigating the anodic oxidation of isopropanol at low pH values with a platinum anode (Fig. 11b) using NaClO₄ as an inert electrolyte.

With PbO₂-anodes the same behaviour can be observed, but the effect is less distinct. Fig. 13 shows this for the oxidation of isopropanol, which was used in our preparative experiments as a cosolvent. Without acrylonitrile, the potential is fairly negative, and acetone is formed at nearly quantitative current efficiency [14, 15]. In the presence of acrylonitrile, the current efficiency for acetone formation decreases to below 50%. The potential is more positive, but acrylonitrile itself is oxidized at even more positive potentials.

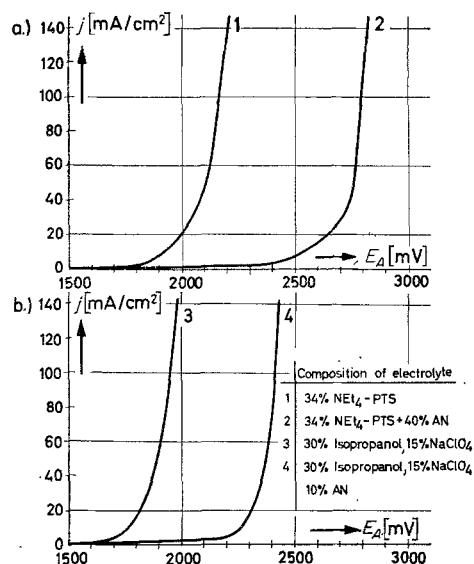


Fig. 11. Anodic shift of current-potential curve with a Pt-anode in the presence of acrylonitrile (35°C). (a) Anodic oxidation of NEt₄-p-toluenesulphonate (pH 9.5) (b) Anodic oxidation of isopropanol (pH 3.5).

The shift of potential with increasing concentration of acrylonitrile is included in Fig. 12.

The low current efficiency for acetone formation in the presence of acrylonitrile indicates, that acetone is partially further oxidized to form CO₂ as the final product. During electrolysis, gas is evolved at an average rate of about 1 ml/A. min.

The gas consists of 80% CO₂, 10% H₂, 5% CO and 5% O₂. The current efficiency for the total oxidation of isopropanol can be calculated from these data to be 35% in the case of batchwise operation.

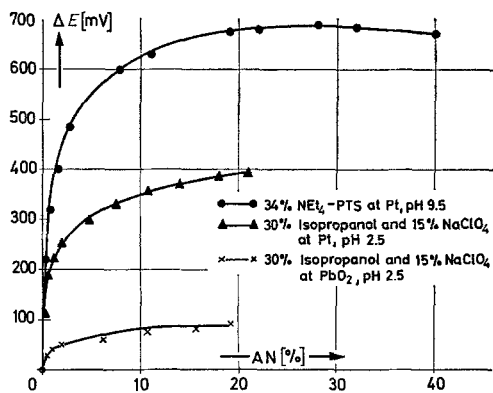


Fig. 12. Anodic shift of potential at 100 mA/cm² on addition of acrylonitrile (35°C).

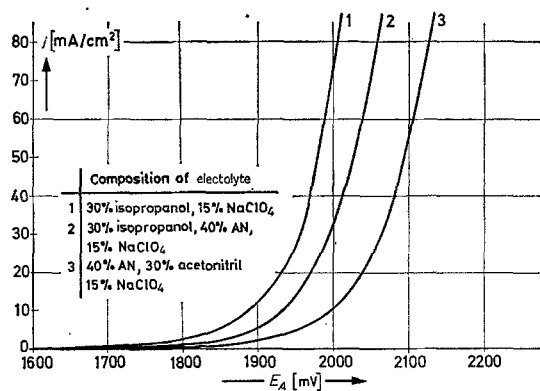


Fig. 13. Anodic shift of current-potential curve with a PbO₂ anode in the presence of acrylonitrile (35°C, pH 2.5).

A main product of the anodic degradation of acrylonitrile would be prussic acid. This compound would be added to acrylonitrile to form succinonitrile quantitatively. Our finding that this compound is mostly generated in yields as low as 0.1% is a further proof that acrylonitrile is only slightly attacked at the anode. On the other hand, the positive shift of the anodic potential in the presence of acrylonitrile is the reason why the oxidation of isopropanol to some extent proceeds beyond the stage of acetone.

4. Conclusion

Electrosynthesis of adiponitrile was carried out in undivided cells. At high salt concentrations (McKee System), the quaternary ammonium salt was strongly decomposed at the anode. The process therefore was uneconomical. Electrolysis at very low salt concentrations in the presence of isopropanol avoids these drawbacks. Cells with a minimum distance between the electrodes must be used. The following advantages have been demonstrated:

1. Yields of adiponitrile of about 90% can be obtained. The energy consumption is less than 3 kWh/kg adiponitrile.
2. Cell design is simple. Cells can easily be scaled up. In spite of the rather low current densities, a high space-time yield can be obtained.
3. Simple continuous operation is possible.
4. Work up is facilitated by the low salt concentrations and is mostly done by distillation.
5. Anodes of lead dioxide are stable. No poisoning of cathodes by anodic corrosion products is possible.

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