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The electrochemical synthesis of aminonitriles
I. H-cell studies with adiponitrile and azelanitrile

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Adiponitrile and azelanitrile were electrochemically hydrogenated to their corresponding aminonitriles in a divided H-cell using Raney nickel powder as the cathode material. The effects of current, temperature, and solvent/supporting electrolyte composition on product selectivities were investigated. Syntheses of the fully hydrogenated diamine by-product increased with increasing current and solution temperature. When a 0.8 M adiponitrile/alcohol/water/ammonium actetate electrolyte was hydrogenated at temperatures of 35–45° C, 6-aminocapronitrile selectivities in the range of 79–97% and current efficiencies of 50–60% were obtained. The optimum applied current was 60 mA for each 2.5 g of catalyst (an apparent current density of 4.8 mA cm^{-2}). For the case of azelanitrile, reaction selectivities for the partially hydrogenated 9-aminononanenitrile product ranged from 80–93%.

1. Introduction

The development of alternative methods for synthesizing the lactam precursors of nylon has long been a subject of interest among organic chemists and polymer engineers. Existing industrial processes for lactam production are capital cost intensive because the reaction pathway for monomer synthesis is complex, involving a number of intermediate reaction and separation steps, for example, the synthesis of caprolactam from benzene or toluene [1–3]. Reaction routes to lactams can be simplified significantly by using dinitrile compounds as the starting material. The key reaction step in this synthesis is the partial hydrogenation of the dinitrile starting material to its corresponding aminonitrile. Aminonitriles can be readily hydrolyzed to amino acids which in turn can be converted into lactam monomer. For example, 6-aminocapronitrile, produced by the partial hydrogenation of adiponitrile, could be hydrolyzed to ε-aminocaproic acid. This acid is converted in the presence of water to nylon-6 by heat. Alternatively, the acid can be converted to caprolactam which in turn can be polymerized to nylon-6 by heating.

High temperature and pressure chemical catalytic processes for the hydrogenation of dinitriles generally produce the corresponding diamine in high yields. The catalytic hydrogenation of adiponitrile, for example, produces hexamethylenediamine with yields of ~99% [4]. This synthesis is carried out using one of a number of catalysts, such as copper-cobalt [5], cobalt oxide [6], iron oxide [7], or cobalt nickel [8]. Typical operating conditions for the reaction are temperatures between 60° C and 200° C and pressures of 300–7000 psi [4]. In 1982, Diamond *et al.* used a rhodium complex catalyst treated with strong base to chemically hydrogenate adiponitrile to aminocapronitrile; an aminonitrile yield of 73% was obtained at 250 psi and 100° C [9]. More recently, Mares *et al.* reported aminocapronitrile selectivities of 94% for the chemical hydrogenation of adiponitrile at a supported rhodium catalyst in the presence of excess ammonia at 1500 psi and 100° C [10].

An alternative approach to chemically hydrogenating dinitrile compounds is to perform an electrocatalytic hydrogenation (reduction) at a low hydrogen overpotential metal powder catalyst, such as Raney nickel or platinum black. In an electrocatalytic reduction, hydrogen is electrochemically generated directly on the catalyst surface by the discharge of protons or water from the adjacent solution. The adsorbed hydrogen then combines with organic reactant to give the reduced product. The driving force for producing hydrogen on the catalyst surface is the electric potential gradient, as opposed to temperature and pressure in chemical catalytic schemes. In this regard, it may be possible to control the hydrogen concentration on the catalyst surface by proper adjustment of the applied current so as to obtain the partially hydrogenated aminonitrile product in high yields. Additional advantages of electrocatalytic hydrogenations over existing chemical process technologies are: 1. elaborate and expensive high pressure reactor systems are not required, 2. both hydrogen and catalyst may be used more efficiently, resulting in lower catalyst loading, and 3. operating temperatures are lower, thus minimizing thermal degradation of the reactant and/or product(s), unwanted homogeneous side reactions, and thermal energy input.

The use of high surface area catalytic powders for organic electrochemical hydrogenations has attracted only limited attention in recent years. Miller and

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Christensen [11] obtained high product yields and current efficiencies for the electro-hydrogenation of phenol to cyclohexanol on rhodium black cathodes in H_2SO_4. Kirilyus and coworkers [12] reported that Raney nickel is highly selective for the electrochemical hydrogenation of pyridine to piperidine in alkaline solutions. Chiba *et al.* [13] demonstrated that Raney nickel could be used to electrochemically hydrogenate a variety of organic compounds, including ketones, nitro-compounds, nitriles, and unsaturated hydrocarbons. Park *et al.* [14] successfully hydrogenated glucose to sorbitol at high current efficiencies and product yields in both batch H-cells and semi-continuous flow reactors. Beck [15] and Sokol'skii [16] have reviewed the subject of electrocatalytic hydrogenation and have compared the electrocatalytic technique with chemical catalytic and direct electron transfer electrochemical processes.

In this paper we report on our preliminary H-cell studies for the electrocatalytic hydrogenation of dinitriles to aminonitriles at a high surface area, low hydrogen overvoltage Raney nickel powder cathode. Two starting materials were investigated; adiponitrile ($CN{-}(CH_2)_4{-}CN$) and azelanitrile ($CN{-}(CH_2)_7{-}CN$). The partial hydrogenation and subsequent hydrolysis of these compounds yield the monomers for nylon-6 and nylon-9, respectively. They also serve as model compounds for the generalized electrochemical hydrogenation of $NC{-}R{-}CN$ to $NH_2{-}CH_2{-}R{-}CN$. All cathode reactions were viewed as two step processes: the electrochemical generation of atomic hydrogen followed by the chemical combination of adsorbed hydrogen (H_{ads}) with either itself or with an organic substrate. For the case of adiponitrile, the primary reaction of interest is the synthesis of 6-aminocapronitrile,

$$4H^+ + 4e^- \longrightarrow 4H_{ads} \qquad (1)$$

$$\underset{\substack{\text{Adiponitrile}\\ \text{(ADN)}}}{NC(CH_2)_4CN} + 4H_{ads} \longrightarrow \underset{\substack{\text{6-aminocapronitrile}\\ \text{(ACN)}}}{NC(CH_2)_5NH_2} \qquad (2)$$

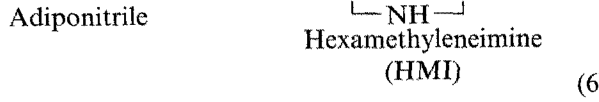
The primary by-product reaction which consumes both electric current and starting material is the complete hydrogenation of adiponitrile to hexamethylenediamine,

$$8H^+ + 8e^- \longrightarrow 8H_{ads} \qquad (3)$$

$$\underset{\text{Adiponitrile}}{NC(CH_2)_4CN} + 8H_{ads} \longrightarrow \underset{\substack{\text{Hexamethylenediamine}\\ \text{(HMD)}}}{H_2N(CH_2)_6NH_2} \qquad (4)$$

A second by-product reaction is the electrochemical synthesis of hexamethyleneimine, a secondary amine,

$$8H^+ + 8e^- \longrightarrow 8H_{ads} \qquad (5)$$



$$\underset{\text{Adiponitrile}}{NC(CH_2)_4CN} + 8H_{ads} \longrightarrow \underset{\substack{\text{Hexamethyleneimine}\\ \text{(HMI)}}}{\underbrace{CH_2(CH_2)_4CH_2}_{NH}} + NH_3 \qquad (6)$$

An additional electrode reaction is the production of hydrogen gas by the combination of electro-generated hydrogen atoms on the catalyst surface:

$$2H_{ads} \longrightarrow H_2(\text{gas}) \qquad (7)$$

Hexamethylenediamine could also be produced by the addition of four hydrogen atoms to a molecule of aminocapronitrile. A similar reaction scheme can be proposed for the electro-hydrogenation of azelanitrile. In this synthesis, the product of interest is 9-aminononanenitrile and the primary by-product is 1,9-diaminononane.

Previous electrochemical studies on the hydrogenation (reduction) of adiponitrile focused, for the most part, on the synthesis of hexamethylenediamine. 6-Aminocapronitrile was viewed as an unwanted minor by-product. Khomyakov *et al.* [17] in 1961 reported their preliminary H-cell experiments for the reduction of adiponitrile at a spongy nickel cathode. The electrolysis of a saturated solution of adiponitrile in an aqueous HCl electrolyte at 20° C produced hexamethylenediamine with a product yield of 60%. Both aminocapronitrile and hexamethyleneimine by-products were detected in electrolysis samples, although the quantities of each were not reported. At temperatures $>25°$ C the aminocapronitrile product was eliminated. The applied current in this study was $10\,A\,dm^{-2}$. Tomilov and coworkers electrochemically hydrogenated adiponitrile in an aqueous solution of 3 N NaOH at 5–8° C and a current density of $100\,mA\,cm^{-2}$ [18]. When the cathode material was iron covered with spongy copper, hexamethylenediamine was the predominant hydrogenation product. When the cathode was composed of iron with spongy nickel, the major hydrogenation product was aminocapronitrile, but the aminonitrile yield was only 56%. In another study, Tomilov *et al.* [19] hydrogenated adiponitrile on a platinum foil cathode which had to be activated with Raney nickel. Hexamethylenediamine was synthesized at a current efficiency of 45% and a product yield of 85% when an alkaline ethanol/water electrolyte was used. Most recently, Chiba *et al.* [13] hydrogenated adiponitrile at a Raney nickel powder cathode in a methanol/sodium methoxide electrolyte. At a temperature of 15° C and an applied current of 0.75 A for each 2.0 g of nickel powder, hexamethylenediamine was produced at a current efficiency of 56% and a yield of 70%. The presence of aminocapronitrile was not reported.

2. Experimental details

A divided glass H-cell electrochemical reactor with a medium porosity glass frit was used in the dinitrile electro-hydrogenation experiments. The anode was a graphite rod and the cathode was approximately 2.5 g of activity W-2 [20] Raney nickel powder. The Raney nickel catalyst was prepared from 50/50 NI/Al powder (Aldrich Chemical Company, Inc.) by standard NaOH leaching techniques [13]. Hydrogen produced and adsorbed on the nickel surface during catalyst activation was removed by soaking the catalyst in a solution of dinitrile starting material and alcohol for 24 h. The nickel powder was then washed thoroughly with alcohol to remove any traces of organic reactant and hydrogenation products. The activated catalyst was placed on a flat nickel sheet current collector at the bottom of the H-cell's cathode compartment. The apparent surface area of the nickel powder bed was 12.5 cm^2 and the bed thickness was ~ 1 mm. Electrical contact to the nickel plate was made by a Teflon® coated 0.125 in diameter nickel rod. The anode and cathode compartments were fitted with dry ice/acetone dewar condensers to minimize evaporative losses and a pH probe was inserted into the H-cell's cathode compartment. The lower portion of the cell was immersed in a constant temperature water bath.

In a typical experiment, the anode and cathode compartments of the H-cell were each initially charged with 50 ml of a dinitrile/alcohol/water/salt solution. The supporting electrolyte for these experiments was either sodium acetate or ammonium acetate (at 0.63 M). The catholyte solution was not purged with inert gas to remove dissolved oxygen, nor was the solvent/supporting electrolyte pre-reduced. Based on the solubility of oxygen in alcohol/water solution [21] less than 2% of the current applied during an electrolysis was consumed by oxygen reduction. A constant d.c. current was supplied by a Hewlett-Packard 6634A power supply and monitored by a Keithley 169 digital multimeter. The total charge passed during an electrolysis was counted with an ESC Model 640 digital coulometer. At the conclusion of an electrolysis a catholyte sample was removed from the H-cell and analyzed for organic reactant, product, and by-products by gas chromatography (Perkin-Elmer Sigma 115). The GC column was composed of 2% Carbowax and 2% KOH on Chromosorb W-AW. Confirmation of adiponitrile reactant and products (hexamethylenediamine, hexamethyleneimine, and 6-aminocapronitrile) and azelanitrile reactant and products (1,9-diaminononane and 9-aminononanenitrile) was achieved by comparison with the retention times of authentic samples available commercially. Calibration of peak areas with standard solutions indicated that adiponitrile reactant and product concentrations could be determined to within 5%. For the case of azelanitrile and its hydrogenation products, the accuracy of the GC analysis technique was estimated to be 8%.

Sufficient current was passed in an electrolysis to convert theoretically ~ 10% of the dinitrile starting material to aminonitrile product (0.4 F mol^{-1} of dinitrile). The goal of the H-cell experiments was to obtain high aminonitrile yields when the concentration of dinitrile starting material was high and the concentration of aminonitrile product was low. No attempt was made to carry out the reaction to completion. The 10% conversion was viewed as a hypothetical conversion per single pass through an industrial-scale Raney nickel flow reactor. Occasionally during an electrolysis the current was interrupted and the cathode solution and Raney nickel powder were stirred. The solution pH was adjusted at this time by addition of acetic acid. The electrolysis was resumed when the catalyst powder settled back onto the nickel plate current collector. A comparison of the charge passed, as noted by the coulometer, and the actual product(s) and reactant concentrations, as determined form the GC analysis, was used to determine current efficiencies and product selectivities. The focus of the experiments was to determine the H-cell operating conditions (applied current, solvent/supporting electrolyte composition, and temperature) which maximized the current efficiency and yield of aminonitrile.

3. Results and discussion

The effect of applied current on the selectivity of the adiponitrile electro-hydrogenation reaction is shown in Fig. 1. Previous adiponitrile studies with a Raney nickel cathode found high diamine yields when the applied currents were high (e.g., 0.375 A g^{-1} of catalyst, from [13]). The focus of our initial electrolyses was to reduce significantly the applied current to a level of 40 to 100 mA for each 2.5 g of catalyst. We anticipated that the concentration of electrogenerated hydrogen on the catalyst surface would be low for this current range and the synthesis of aminonitrile product would be favoured. In these experiments the solvent was a 70/30 volume % ethanol/water solution containing 0.63 M sodium actetate. The solution temperature was 45° C, the solution pH was 7–8, and the initial adiponitrile (ADN) concentration was 0.8 M.

The highest reaction selectivity for aminocapronitrile (87%) was achieved with an applied constant current of 60 mA (an apparent current density of 4.8 mA cm^{-2}). At 60 mA, the molar ratio of aminocapronitrile (ACN) to hexamethylenediamine (HMD) in the final catholyte was 10/1. This yield is considerably higher than that obtained in previous studies. The concentration of HMD by-product increased with increasing current, thus, substantiating our hypothesis that the synthesis of diamine is favoured

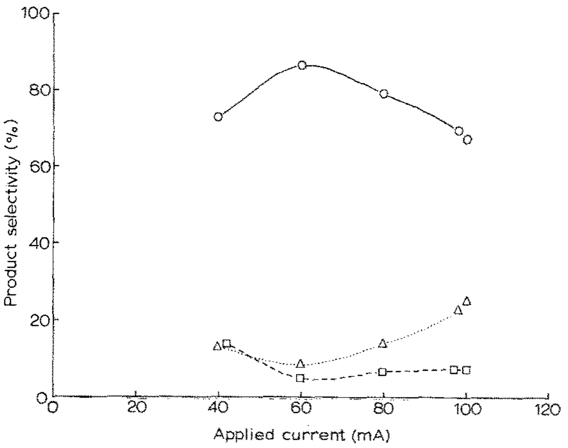


Fig. 1. The effect of current on the selectivity of the adiponitrile hydrogenation reaction ($T = 45°$ C). 70/30 vol % ethanol/water solvent, 0.63 M sodium acetate supporting electrolyte, pH = 7–8, 0.8 M initial adiponitrile concentration, charge passed = 0.4 F mol^{-1}. (○) ACN, (△) HMD, (□) HMI.

when the concentration of electro-generated hydrogen on the nickel surface is high. The low ACN selectivity at 40 mA was due to the high rates of both secondary amine (HMI) and HMD formation. In the high temperature and pressure chemical catalytic hydrogenation of adiponitrile to hexamethylenediamine, secondary amine synthesis is suppressed by an alkaline solution medium (addition of NaOH) [6] or by the addition of NH_3 [22]. When hydrogen is electrogenerated by the discharge of protons or water molecules, the solution pH in the immediate vicinity of the cathode increases. In principle, the presence of this alkaline region should inhibit HMI formation. The secondary amine results in Fig. 1 suggest that the combination of low current (40 mA) and periodic stirring prevented the OH^- ion concentration in the nickel bed from attaining the level needed to suppress HMI synthesis. For currents equal to or greater than 60 mA, the HMI selectivity was insensitive to current and remained relatively constant at ~7%.

A mass balance calculation was performed for each H-cell experiment. In a mass balance determination, the total moles of unreacted adiponitrile, organic products, and by-products present at the conclusion of an electrolysis was compared to the initial moles of adiponitrile in the reactor. Such a calculation was used to check for the presence of additional by-products which may not have been detected by gas chromatography. In most experiments, mass balance calculations could account for 94–99% of the starting adiponitrile. In no experiment was the mass balance below 87%. No unknown GC peaks were observed when electrolysis samples were analyzed and it was concluded that only reactions given by Equations 1-7 were occurring in the cathode compartment of the H-cell when adiponitrile was electrochemically hydrogenated.

A charge balance calculation was also carried out for each H-cell electrolysis. The total number of coulombs necessary to synthesize the moles of organic products detected at the conclusion of an experiment was compared to the actual charge passed, as noted by the coulometer. Charge balances less than 100% were attributed to the electrochemical generation of hydrogen gas. Charge balances and aminocapronitrile current efficiencies are plotted for different applied currents in Fig. 2. Maximum utilization of electro-generated hydrogen was achieved at 80 mA, where only ~14% of the total current was lost to H_2 gas evolution. 80 mA was not considered to be the optimum applied current, however, because the aminocapronitrile/hexamethylenediamine concentration ratio was low (5.7/1) and the concentration of secondary amine was slightly higher than that at 60 mA. The low charge balance at 100 mA implies that the hydrogen generation rate exceeded the rate at which hydrogen added to the organic substrate; the net result being excessive hydrogen gas evolution. Low applied currents should reduce H_2 evolution losses, but the low charge balance at 40 mA does not support this hypothesis. The high rates of hydrogen gas formation at 40 mA can not be explained at this time. Although 4.8 mA cm^{-2} is a low apparent current density, it may be possible to achieve high aminocapronitrile yields at higher current densities in a Raney nickel flow reactor where the aminonitrile product is quickly dispersed into the bulk electrolyte. Increasing the initial adiponitrile concentration may also allow for high current densities. Such experiments were not performed in this study. It should be noted that the actual current density on the 2.5 g of Raney nickel powder is very low (1.6×10^{-5} mA cm^{-2} based on a Raney nickel surface area of 100 m^2 g^{-1} and a current of 40 mA for each 2.5 g of catalyst), but it is the apparent current density which is used to design and cost packed bed electro-organic reactors.

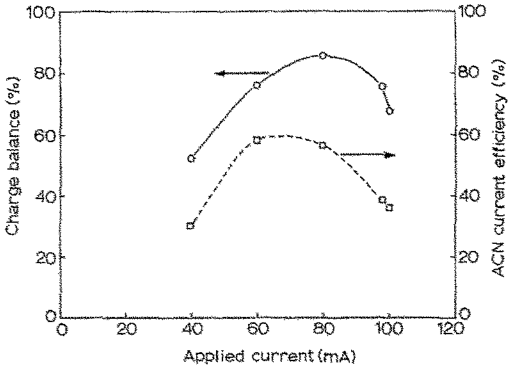


Fig. 2. The effect of the applied current on the aminocapronitrile (ACN) current efficiency and the charge balance of the adiponitrile hydrogenation reaction (same reaction conditions as Fig. 1).

Based on our primary criteria of a high ACN/HMD concentration ratio in the final catholyte, the optimum current was 60 mA (4.8 mA cm^{-2} of apparent cathode area). At this current the ACN current efficiency was 58.3% with 23.9% of the current consumed by hydrogen evolution, 6.4% consumed by HMI formation, and 11.4% consumed by the synthesis of HMD. At higher adiponitrile conversion rates the aminocapronitrile current efficiency may decrease due to lower concentrations of starting material and higher concentrations of the partially hydrogenated aminonitrile product. Raney nickel flow reactor experiments are currently being performed to study this effect. The results of this work will be the subject of a future publication.

Methanol/water and t-butanol/water mixtures were also investigated as solvents for the aminocapronitrile synthesis. t-Butanol is the preferred alcohol because it is more difficult to oxidize anodically than water and, thus, is suitable for use in an undivided Raney nickel flow reactor. In these experiments the sodium acetate supporting electrolyte was replaced by ammonium acetate (at 0.63 M). There is some evidence in the literature to suggest that ammonium salts improve product yields when nitrile compounds are reduced to their corresponding amines [23]. In addition, we believe that the presence of ammonium ions may further decrease secondary amine by-product formation. In the highly alkaline solution region adjacent

Table 1. Effect of methanol/water solvent composition on the electrochemical hydrogenation of adiponitrile

Solvent composition (vol % methanol/water)	95/5	90/10	85/15	80/20	70/30
Selectivity (%)					
ACN	96	97	91	90	84
HMD	1	2	4	2	7
HMI	2	2	5	8	10
Charge balance (%)	66	67	67	78	80
ACN current efficiency (%)	62	63	55	65	58

Divided H-cell; initial catholyte: 50 ml of 0.8 M adiponitrile and 0.63 M ammonium acetate; $T = 40°C$; pH = 8–10; applied current = 60 mA; charge passed: 1500 Coulombs ($0.4\,F\,mol^{-1}$)

to the nickel catalyst, NH_4^+ will combine with hydroxyl ions and produce ammonia,

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O \qquad (8)$$

According to Equation 6, the presence of ammonia inhibits hexamethyleneimine formation. Tables 1 and 2 list the adiponitrile hydrogenation product selectivities, charge balances, and aminocapronitrile current efficiencies for methanol/water/ammonium acetate and t-butanol/water/ammonium acetate electrolytes, respectively. The operating temperature for these H-cell electrolyses was 40° C, the applied current was 60 mA, and the initial adiponitrile concentration was 0.8 M. From the results of the methanol experiments, it can be seen that the 95/5 and 90/10 alcohol/water solutions gave the highest ACN selectivity. On average, HMI by-product formation was reduced by more than one-half, as compared to the ethanol/sodium acetate results in Fig. 1, presumably due to the beneficial effect of ammonium cations. Diamine by-product concentrations also decreased substantially with selectivities of 1–2% and ACN/HMD molar ratios of 81/1 (95/5 solvent) and 64/1 (90/10 solvent). It is unclear at the present time whether the use of methanol or ammonium acetate caused the dramatic increase in ACN product selectivity. The charge balances listed in Table 1 indicate that hydrogen losses as H_2 gas were reduced by one-half when the solvent contained more than 20 vol % water.

Table 2. Effect of t-butanol/water solvent composition on the electrochemical hydrogenation of adiponitrile

Solvent composition (vol % t-butanol/water)	75/25	65/35	50/50	25/75
Selectivity (%)				
ACN	79	83	85	87
HMD	19	13	11	7
HMI	3	3	4	6
Charge balance (%)	90	91	70	65
ACN current efficiency (%)	58	65	52	50

Divided H-cell; initial catholyte: 50 ml of 0.8 M adiponitrile and 0.63 M ammonium acetate; $T = 40°C$; pH = 8–10; applied current = 60 mA; charge passed: 1500 Coulombs ($0.4\,F\,mol^{-1}$)

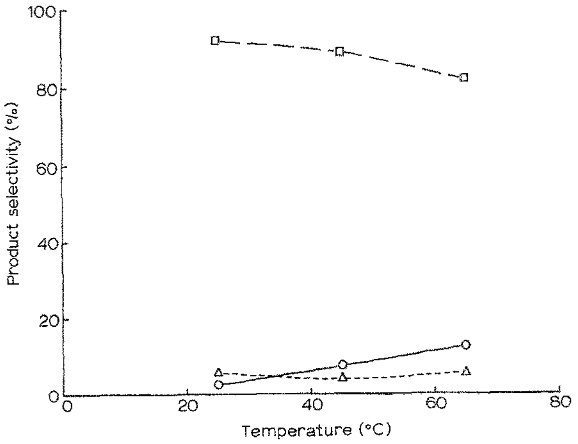


Fig. 3. The effect of temperature on the aminocapronitrile (ACN), hexamethylenediamine (HMD), and hexamethyleneimine (HMI) selectivities for a 70/30 vol % ethanol/water solvent. (60 mA current, 0.63 M ammonium acetate supporting electrolyte, 0.8 M initial adiponitrile concentration, pH = 8–10, charge passed = $0.4\,F\,mol^{-1}$). (○) HMD, (△) HMI, (□) ACN.

The results of the t-butanol experiments in Table 2 show a low reaction selectivity for HMI by-product, but the rate of formation of diamine is greater than that found with methanol/water solutions. In terms of ACN product selectivity, a 25/75 volume % t-butanol/water solvent gave the best results, with a final ACN/HMD mole ratio of 12/1. Unfortunately, the final charge balance and ACN current efficiency for this solvent were low (65% and 50%, respectively). In contrast to the methanol/water solvent results in Table 1, hydrogen evolution decreases as the water content in the solvent increases. Based on both the product selectivity and charge balance data, the optimum composition for a t-butanol/water solvent is a solution containing between 50 and 65 vol % alcohol.

The effect of temperature on the performance of the adiponitrile hydrogenation reaction is shown in Figs 3–5. Two different solvents were used in these experiments: 70/30 vol % ethanol/water and 60/40 vol % t-butanol/water. The supporting electrolyte was 0.63 M ammonium acetate, the applied current was 60 mA,

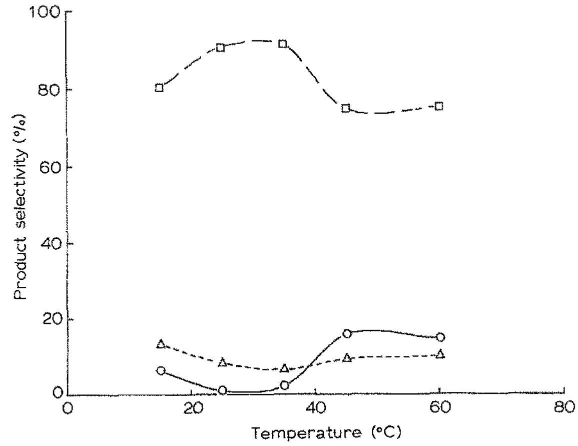


Fig. 4. The effect of temperature on the aminocapronitrile (ACN), hexamethylenediamine (HMD), and hexamethyleneimine (HMI) selectivities for a 60/40 vol % t-butanol/water solvent (60 mA current, 0.63 M ammonium acetate supporting electrolyte, 0.8 M initial adiponitrile concentration, pH = 8–10, charge passed = $0.4\,F\,mol^{-1}$). (○) HMD, (△) HMI, (□) ACN.

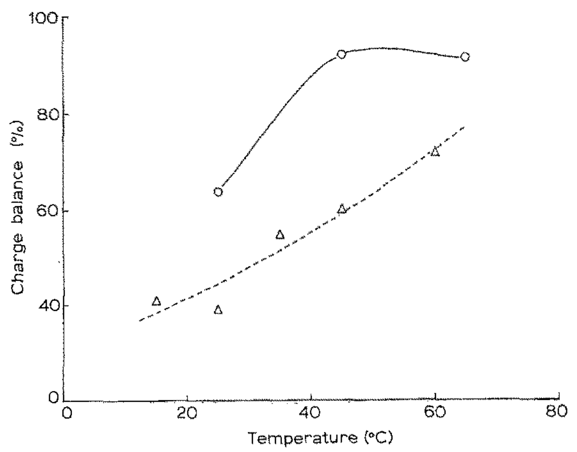


Fig. 5. The effect of solution temperature on the adiponitrile hydrogenation charge balance. (○) 70/30 vol % ethanol/water solvent: (△) 60/40 vol % t-butanol/water solvent (H-cell reaction conditions are the same as Fig. 3).

and the pH was between 8 and 10. Solution temperatures ranged from 15 to 65° C. ACN, HMD, and HMI product selectivities are plotted as a function of solution temperature in Fig. 3 (ethanol/water) and Fig. 4 (t-butanol/water). For both alcohol solvent systems, the yield of ACN product decreases with increasing temperature. The optimum temperature for the partial hydrogenation of adiponitrile was found to be between 25 and 35° C. The low ACN yield at temperatures ⩾ 45° C for the ethanol/water system was due to high rates of hexamethylenediamine formation. A similar temperature trend is seen in Fig. 4 for both HMD and HMI by-products when the solvent was a mixture of t-butanol and water. The poor results at 15° C were due primarily to an unacceptably high rate of secondary amine formation. The general trend in the charge balance vs. temperature results (Fig. 5) shows an improvement in the utilization of electro-generated hydrogen with increasing solution temperatures. This finding is not unexpected; higher solution temperatures increase the rate of hydrogen addition to the organic substrate, thus lowering the concentration of adsorbed hydrogen on the catalyst surface and reducing the likelihood of hydrogen atoms combining to form H_2. In terms of ACN current efficiency, the optimum solution temperature was 35° C for a t-butanol/water solution (46% current efficiency) and 45° C for an ethanol/water system (73% current efficiency).

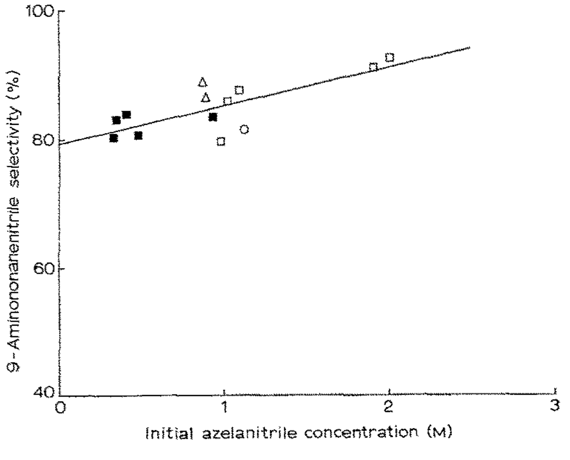


Fig. 6. The effects of initial azelanitrile concentration and solution temperature on the selectivity of partially hydrogenated 9-aminononanenitrile (90/10 vol % methanol/water solvent, 0.63 M ammonium acetate supporting electrolyte, 60 mA current, pH = 7–10). (△) T = 25° C, (□) T = 45° C, (○) T = 55° C, (■) T = 61° C.

The product yield results from 13 azelanitrile H-cell hydrogenation experiments are shown in Fig. 6. In these electrolyses the solution temperature was varied from 25 to 61° C and the initial azelanitrile concentration ranged from 0.345 to 2.0 M. The applied current for all experiments was 60 mA and the solvent/supporting electrolyte was a 90/10 volume % methanol/water solution containing 0.63 M ammonium acetate. The catholyte pH was maintained between 7 and 10 by addition of acetic acid. The only products detected by GC analysis of the final electrolysis samples were 9-aminononanenitrile and 1,9-diaminononane.

On average, 1730 coulombs were passed in each hydrogenation experiment. This charge reperesents a 26% theoretical conversion of dinitrile to aminonitrile for the 0.345 M azelanitrile electrolysis and a 4.5% conversion when the initial azelanitrile concentration was 2.0 M. In all of the experiments, 9-aminononanenitrile was the predominant hydrogenation product. Mass balance calculations at the conclusion of an experiment could account for all the initial starting material. Aminononanenitrile selectivities ranged from 80 to 93%. The highest selectivities were obtained when the solution temperature was either 25 or 45° C. As was the case for adiponitrile, the diamine product of azelanitrile was favoured at solution temperatures greater than 45° C. We attribute the low aminononanenitrile selectivities for 0.345 M starting material to the high relative conversion rates of dinitrile starting material to aminonitrile product. At the conclusion of a 2.0 M experiment, the concentration ratio of azelanitrile to aminononanenitrile was ~10/1, whereas this concentration ratio at the end of a 0.345 M electrolysis was ~4/1. As the dinitrile/aminonitrile concentration ratio in the catholyte falls, we believe that the probability of hydrogen adding to aminononanenitrile increases and more 1,9-diaminononane is synthesized.

4. Conclusions

Two dinitrile compounds (adiponitrile and azelanitrile) were each electrochemically hydrogenated to their corresponding aminonitriles in a batch H-cell using Raney nickel powder (activity W-2) as the cathode material. The effects of applied current (40 mA – 100 mA for each 2.5 g of nickel), solution temperature (25–65° C), and solvent composition (ethanol/water, methanol/water, and t-butanol/water) on product selectivities and aminonitrile current efficiencies were investigated. For all conditions examined, the partially hydrogenated aminonitrile product was obtained in high yields, with product selectivities in the range 79–97%. Synthesis of the fully hydrogenated diamine by-product increased with increasing current (currents > 60 mA for each 2.5 g of catalyst) and solution temperature (temperatures $\geqslant 45°$ C). The optimum current was found to be 60 mA for each 2.5 g of nickel.

For the case of adiponitrile, the presence of an ammonium ion containing supporting electrolyte lowered the rate of formation of secondary amine by-product (hexamethyleneimine) and improved the yield of 6-aminocapronitrile. The optimum conditions for the hydrogenation of adiponitrile to aminocapronitrile, based on all H-cell experiments, was obtained with a 95/5 vol % methanol/water solvent containing 0.63 M ammonium acetate supporting electrolyte. When the current was 60 mA for each 2.5 g of nickel and the solution temperature was 40° C, the molar product selectivities at $0.4\,\mathrm{F\,mol^{-1}}$ were: 96% for aminocapronitrile, 1% for hexamethyleneimine, and 2% for hexamethyleneimine. Some 34% of the current was consumed by hydrogen gas evolution and the overall aminocapronitrile current efficiency was found to be 62%.

When azelanitrile was electrochemically hydrogenated at 60 mA for each 2.5 g of catalyst, only 9-aminononanenitrile (the partially hydrogenated product) and 1,9-diaminononane (the completely hydrogenated by-product) were detected by GC analysis. The solvent/supporting electrolyte for these electrolyses was a 90/10 vol % methanol/water solution containing 0.63 M ammonium acetate. For initial azelanitrile concentrations of 0.345–2.0 M and solution temperatures of 25–61° C, 9-aminononanenitrile selectivities ranged from 80 to 93%.

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