BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1316—1321 (1969)

A Mechanistic Approach to the Electrolytic Reductive Dimerization of Acrylonitrile

Teruzo ASAHARA, Manabu SENŌ and Takeshi ARAI*1

Institute of Industrial Science, The University of Tokyo, Minato-ku, Tokyo

(Received February 24, 1968)

The electrolytic reductive dimerization of acrylonitrile was investigated extensively especially in order to obtain some mechanistic information. The essential point of this reaction exists in the selective formation of adiponitrile under relatively wide conditions and this cannot be explained by a normal kinetic treatment based on the reaction scheme which has been accepted as probable. The heterogenuity in acrylonitrile concentration in the reaction system is assumed and the kinetic formulas are modified. This treatment explains the experimental results very satisfactorily. In order to confirm this mechanistic scheme, the effects of temperature, pH and solvents on the yield of reaction products were examined. All the results are consistent with the proposed mechanism.

Recently Baizer[1] *et al.* carried out extensive studies on the electro-reductive dimerization of acrylonitrile and other vinyl compounds. Their work is limited to examining the conditions for exclusive preparation of hydro-dimers and the reaction mechanism for this process is not yet clarified in detail. Therefore, the extensive studies have been designed to examine the effect of the experimental conditions on the electro-reductive dimerization of acrylonitrile to get some mechanistic information for this process. In the present paper, the effects of current densities, concentrations of acrylonitrile, temperatures, pH and solvents on the formation of adiponitrile, propionitrile and oligomers from acrylonitrile will be examined and discussed.

Experimental

Apparatus. As shown in Fig. 1, the reaction cell is a cylindrical separable flask of the area of the bottom of 0.3 dm^2, equipped with an inlet tube for N_2 gas, a thermometer, a glass electrode for the measurement of pH value, a platinum anode, a separatory funnel and a cooler with dry-ice acetone mixtures. There are a mercury pool at the bottom as the cathode, and a junction connected with a saturated calomel electrode. The separatory membrane was not used in this apparatus.

*1 Present address: Institute for Fats and Oils, Japan Fats and Oils Co., Ōhamacho, Amagasaki.

1) M. M. Baizer, *J. Electrochem. Soc.*, **111**, 215 (1964); *Tetrahedron Letters*, **1963**, 973; *J. Org. Chem.*, **29**, 1670 (1964).

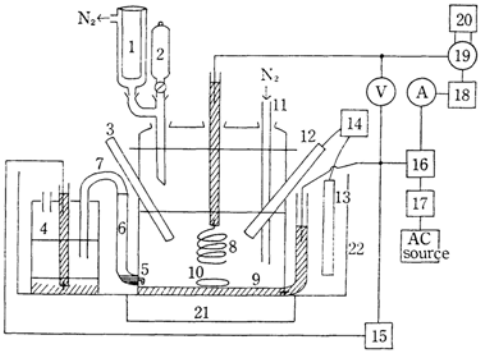

Fig. 1. Apparatus for electrolysis.
1. Dry-ice acetone cooler, 2. Dropping funnel, 3. Thermometer, 4. Saturated calomel electrode, 5. Liquid junction, 6. Sat. KCl aq. solution, 7. Sat. KCl-Agar bridge, 8. Platinum cathode, 9. Mercury anode, 10. Stirrer, 11. N_2 gas inlet, 12. Glass electrode, 13. Temp. calibrating electrode, 14. pH meter, 15. Vacuum voltmeter, 16. Constant voltage supply, 17. Stabilizer, 18. Mercury coulometer, 19. Standard resister (1Ω), 20. Recorder, 21. Magnetic stirrer, 22. Thermostat

Chemicals. Tetraethylammonium *p*-toluenesulfonate (QAS), used as a supporting electrolyte, was prepared according to the method reported by Baizer. It was confirmed by IR spectrum to contain neither amine nor ester. Commercially available acrylonitrile was used after treatment with calcium chloride followed by distillation twice. Calcium sulfate and methylene dichloride were used without further treatments.

Electrolytic Reduction. A QAS solution was placed into the electrolytic cell and, while N_2 gas was passed through, a definite amount of acrylonitrile was added and then the electrolysis was initiated, the temperature being kept constant. The formation of precipitates in a small quantity was observed in a cathode region during electrolysis. After a definite period of electrolysis, the electrolysed soltuion was neutralized, cooled with water and transferred into a separatory funnel. The 200 m*l* of water was added and, after the precipitates were removed, the water layer was extracted four times with each 50 m*l* of methylene dichloride, and the extracts were combined to the acrylonitrile layer. The combined solution was washed with water twice, dried with calcium sulfate, and methylene dichloride was removed by distillation. The residue was analysed by gas chromatography (Shimadzu GC-1C, column Tween 80 on Chromosorb P).

The precipitates were purified twice through reprecipitation with dimethylformamide and water and analysed by IR and vapor pressure osmometer measurements.

Electrolytic Potential and Electrolytic Current. The relation of the electrode potential and the electrolytic current to the applied voltage are shown in Fig. 2 in the cases of the absence and the presence of acrylonitrile. By the addition of acrylonitrile the cathode potential decreases significantly and the electrolytic current increases. There is some difference between the reduction potentials of acrylonitrile and QAS, as shown in

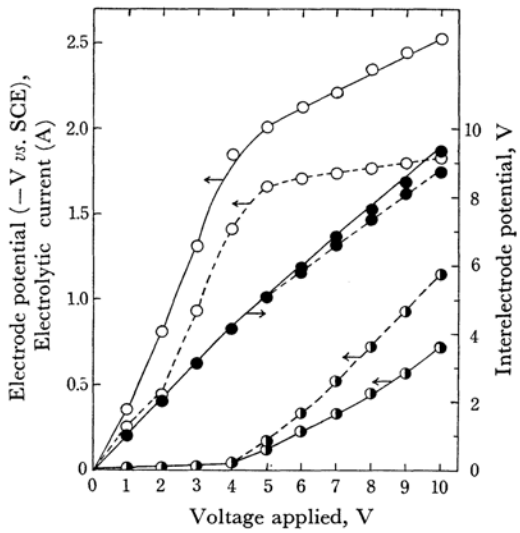

Fig. 2. Relations between electrode potential, electrolytic current and applied voltage (30°C).
○ electrode potential, ● interelectrode potential, ◑ electrolytic current
Solid line, 55.7% QAS (pH 5.5)
Dotted line, AN 30.0 g + 55.7% QAS 79.0 g (pH 5.7)

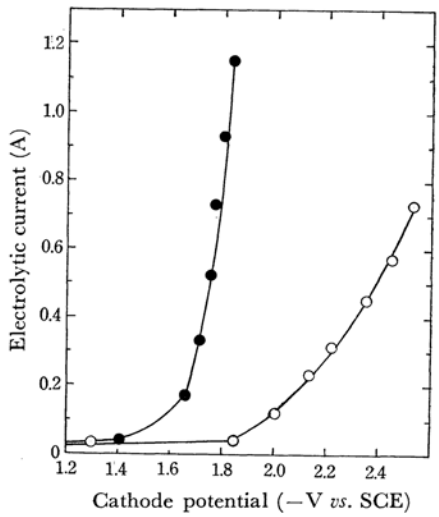

Fig. 3. Current-potential curves.
○ QAS soln. ● (QAS+acrylonitrile) soln.

Fig. 3.

Conditions of Electrolysis. In all the experiments, the total volume of the reaction solution was 100 m*l*. The current efficiency was calculated under the assumption that the theoretical electric quantity of 2 faradays is required for the formation of each 1 mol of adiponitrile.

Products of Electrolysis. The formation of propionitrile and adiponitrile was detected by GLC and IR measurements. The product precipitated from water was confirmed to be oligomers of acrylonitrile by the

Table 1. Conditions for electrolysis

No.	Acrylonitrile g	Acrylonitrile wt%	QAS soln.[1] g	Temp.[2] °C	pH	Voltage V	Cathode potential −V *vs.* SCE	Current density A/dm²	A·hr[3] ×3600 coul.
1	30.0	27.5	79.0	31.7	6—2	7.0	1.7—1.8	1.45	3.05
2	30.0	27.5	79.0	31.7	6—2	8.0	1.7—1.8	2.12	4.45
3	30.0	27.5	79.0	32.5	6—2	9.0	1.7—1.8	2.74	5.75
4	30.0	27.5	79.0	34.0	6—2	10.0	1.8—1.9	3.55	7.45
5	30.0	27.5	79.0	33.5	6—2	10.8	1.7—1.8	4.40	9.24
6	30.0	27.5	79.0	32.5	6—2	11.8	1.6—1.7	5.17	7.75
7	37.4	35.0	69.4	33.5	6—2	10.0	1.7—1.8	3.57	5.36
8	41.4	40.0	62.0	33.5	6—2	10.0	1.7—1.9	3.65	5.48
9	46.0	45.0	56.2	34.0	6—2	10.0	1.8—1.9	3.66	5.50
10	50.6	50.0	50.6	33.5	6—2	10.0	1.8—1.9	3.56	5.33
11	41.4	40.0	62.0	33.5	6—2	11.8	1.8—1.9	5.23	7.85
12	30.0	27.5	79.0	18.2	6—2	10.0	1.8—1.9	2.79	4.18
13	30.0	27.5	79.0	24.3	6—2	10.0	1.8—2.0	3.18	4.77
14	30.0	27.5	79.0	29.0	6—2	10.0	1.9—2.0	3.47	5.21
15	30.0	27.5	79.0	34.0	6—2	10.0	1.8—1.9	3.55	7.45

1) 55.7% QAS aq. solution. 2) Maximum temp., thermostat temp., 30°C (Nos. 1—11, 15), 15°C (No. 12), 20°C (No. 13), 25°C (Nos. 14, 16, 18—22), 22°C (Nos. 17, 23)
3) Time, 7 hr (Nos. 1—5, 15), 5 hr (Nos. 6—11, 12—14, 16—22), 3hr (No. 23).

IR measurement and the average degree of polymerization was estimated to be 3—5 from the vapor pressure osmometer using methyl ethyl ketone as a solvent.

Results and Discussion

Baizer[1] has established the process of electrolytic preparation of adiponitrile from acrylonitrile. The essential point of this method exists in the use of McKee's salt. Acrylonitrile dissolves or disperses into water to 4.5 wt% at room temperature in the presence of McKee's salt and McKee's salt is almost inactive to the electrode reaction even in the range of cathode potential sufficiently high for the reduction of acrylonitrile. The reaction conditions, under which adiponitrile is a main product, were elucidated by Baizer as follows; the acrylonitrile concentration is in the range from 10 to 40 wt% in water and the cathode potential is about −2.0 V *vs.* SCE.

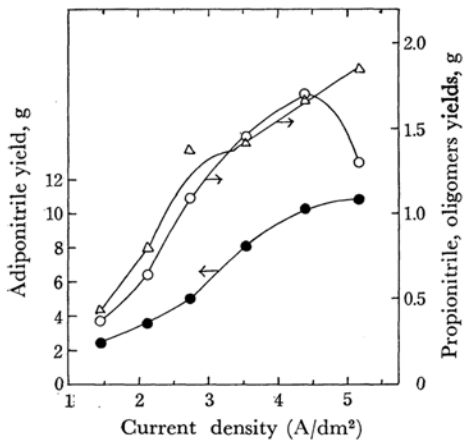

Fig. 4. Relation of yields and current density.
● Adiponitrile, ○ Propionitrile, △ Oligomers

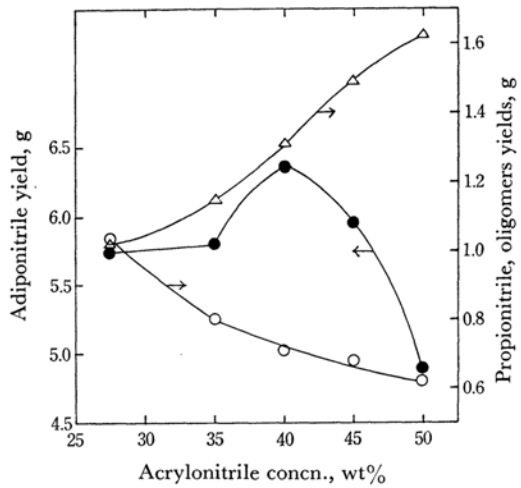

Fig. 5. Relation of yields and acrylonitrile concentration.
● Adiponitrile, ● Propionitrile, △ Oligomers

Although the principal feature of this reaction became clear by Baizer's pioneer work, further examination would be necessary to get some mechanistic information. In Figs. 4 and 5, the effect of current densities and acrylonitrile concentrations on the yields of reaction products are shown in the vicinity of optimum conditions for the adiponitrile formation.

It is considered that these results confirm the following reaction scheme which was originally suggested by Baizer and modified in part in the present work;

$$CH_2CHCN \xrightarrow[k_1]{2e} \overset{\ominus}{C}H_2\overset{\ominus}{C}HCN \longrightarrow$$

$$\begin{cases} \xrightarrow[k_2]{2H^+} CH_3CH_2CN \\ \xrightarrow[k_3]{AN} NC\overset{\ominus}{C}HCH_2CH_2\overset{\ominus}{C}HCN \longrightarrow \end{cases}$$

$$\begin{cases} \xrightarrow[k_4]{2H^+} NCCH_2CH_2CH_2CH_2CN \\ \xrightarrow[k_5]{AN} \text{oligomers} \end{cases}$$

The initial step of 2-electron reduction is confirmed by polarographic examination.[2)]

The kinetic treatment under the assumption of stationary state for the intermediate dianions leads the following formula for the formation rates of propionitrile (PN), adiponitrile (ADN) and oligomers (olig) of acrylonitrile.

$$\frac{d[PN]}{dt} = \frac{k_1k_2[AN][H^+]^2I}{k_2[H^+]^2+k_3[AN]}$$

$$\frac{d[ADN]}{dt} = \frac{k_1k_3k_4[AN]^2[H^+]^2I}{(k_2[H^+]^2+k_3[AN])(k_4[H^+]^2+k_5[AN])}$$

$$\frac{d[olig]}{dt} = \frac{k_1k_3k_5[AN]^3I}{(k_2[H^+]^2+k_3[AN])(k_4[H^+]^2+k_5[AN])}$$

where k_1, k_2,$\cdots$ are the rate constants corresponding to each step of reactions, and I denotes the current density.*2 The effect of the current density and the acrylonitrile concentration as shown in figures above are explained by these formulas. However, there is one important point that is completely inconsistent with these kinetic results, which were derived under the assumption of the uniformity through the reaction system. That is, this treatment leads to the result that the rate of formation of PN is always larger than that of ADN, if the ratio of rate constants k_2/k_3 is comparable to the ratio k_4/k_5, but Baizer's result and the present result show the reverse result; the main product in this reaction system is adiponitrile even when the AN concentration is so low as 10% as shown by Baizer.

This experimental result is confirmed more clearly from the investigation for the rates of formation of PN and ADN, the result of which is shown in Fig. 6.

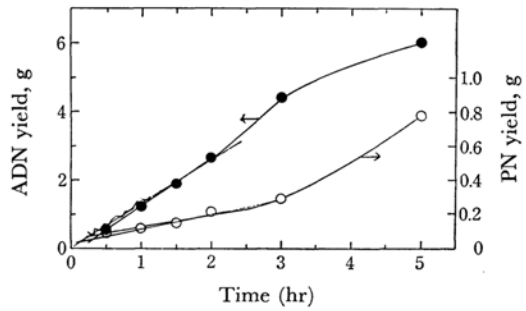

Fig. 6. Rates of formation of propionitrile and adiponitrile.

If the reaction mechanism as mentioned above would be valid, this essential behavior should be interpreted from the following reasons. Propionitrile is formed through the successive attacks of protons or proton donors to the dianion $\overset{\ominus}{C}H_2\overset{\ominus}{C}HCN$ at any positions and, on the other hand, adiponitrile is formed only through the attack of acrylonitrile to the dianion at the β-position to the nitrile group. Therefore, to explain the present result, it should be considered that the protonation ability in this system is very weak or the propionitrile dianion would be easily attacked by acrylonitrile at the β-position under the present circumstance.

In order to examine the first possibility, the effect of pH was investigated. The result is shown in Table 2. In general, the yield of propionitrile is high under the acidic condition and the yield of adiponitrile is high under the basic condition, as expected, but there is no definite quantitative correlation between pH and the product yield, and the property of each reagent used for the adjustment of pH clearly gives rise to a characteristic behavior. For example, acetic acid depresses very strongly the formation of adiponitrile, but sulfuric acid has no remarkable effect. This result reveals that the protonation ability is influenced by the physical situation of proton donors in the present system.

Moreover, it would be considered that this physical situation leads to the result that adiponitrile is formed as a main product in this reaction system. That is, taking this situation into consideration, we must modify the kinetic formula derived above under the assumption of the uniformity of the reaction system. Presumably the concentration of acrylonitrile is different in positions, *i. e.* the electrode surface and the bulk of solution, and the steps 2 and 3 of the reaction occur at the cathode surface and the steps 4 and 5 occur in the bulk. The kinetic treatment affords the following formulas;

2) T. Asahara, S. Hayano, M. Senō and H. Kaneko, *Denki Kagaku (J. Electrochem. Soc. Japan)*, **35**, 882 (1967).

*2 In these equations, the exponent 2 on the proton concentration comes from the overall reaction formula in which one dianion reacts with two protons. But the rate-determining step in this protonation reaction is not clear and, therefore, the reaction order regarding protons is not conclusive.

TABLE 2. EFFECTS OF pH ON ELECTROLYSIS OF ACRYLONITRILE

No.[1]	Reagent for pH adjust	pH	Products: Adiponitrile g	Adiponitrile %[2]	Propionitrile g	Propionitrile %	Oligomers g	Oligomers Mol wt[3]	Total yield g	Yield ratio, g/g ADN/PN	Yield ratio, g/g ADN/olig
16	none	6.2	5.42	46.5	0.76	13.8	1.08	160	7.26	7.1	5.0
17	none	6.2	7.76	49.3	0.60	8.0	1.70	171	10.06	12.9	4.6
18	H_2SO_4	2.2	3.60	33.8	0.81	16.1	1.05	144	5.46	4.4	3.4
19	CH_3COOH	4.0	0.55	5.2	1.12	22.4	0.15	104	1.82	0.5	3.7
20[4]	Et_3N	8.2	6.21	53.2	0.79	14.3	1.49	147	8.47	7.9	4.2
21[4]	Et_3N	10.5	5.77	55.8	0.73	14.9	1.88	228	8.38	7.9	3.1
22	KOH	10.5	7.20	61.1	0.09	1.6	2.15	144	9.44	80.0	3.4
23	KOH	10.1	6.13	63.9	0.11	2.4	1.33	158	7.57	55.8	4.6

1) Acrylonitrile 41.4 g (40.0 wt%), QAS 55.7% aq. soln. 62.0 g. Voltage 10.0 V (Nos. 17 and 23, 11.8 V), Cathode potential 1.8—1.9 V *vs.* SCE, Time 5 hr (No. 23, 3 hr), Temp., 28—29°C.
2) Current efficiency
3) From vapor pressure osmometer
4) Trace of biscyanoethyl ether was dectected.

$$\frac{d[PN]}{dt} = \frac{k_1k_2[AN]^*[H^+]^*I}{k_2[H^+]^*+k_3[AN]^*}$$

$$\frac{d[ADN]}{dt} = \frac{k_1k_3k_4[AN]^{*2}[H^+]^2I}{(k_2[H^+]^{*2}+k_3[AN]^*)(k_4[H^+]^2+k_5[AN])}$$

$$\frac{d[olig]}{dt} = \frac{k_1k_3k_5[AN]^{*2}[AN]I}{(k_2[H^+]^{*2}+k_3[AN]^*)(k_4[H^+]^2+k_5[AN])}$$

where [ ] stands for the concentration in the bulk and [ ]* stands for that at the cathode surface.

If it is assumed from the above consideration that $[AN]^*>[AN]$ and $[H^+]^*<[H^+]$, the experimental behavior is well explained. For instance, if the concentration of acrylonitrile is larger than that of protons in the bulk, the yield ratio of adiponitrile to propionitrile is expressed from the above formulas as follows;

$$\frac{d[ADN]}{d[PN]} = \frac{k_3k_4}{k_2}\frac{[H^+]^2[AN]^*}{[H^+]^{*2}(k_4[H^+]^2+k_5[AN])} \simeq \frac{k_3k_4}{k_2k_5}\left(\frac{[H^+]}{[H^+]^*}\right)^2\left(\frac{[AN]^*}{[AN]}\right)$$

From the assumption that the ratio k_2/k_3 is in a comparable order to the ratio k_4/k_5 it could be expected that adiponitrile becomes a main product in this reaction system if the adsorption of acrylonitrile at the cathode surface takes place to a great extent.

This assumption seems to be probable from the reason that the cathode surface is active for the adsorption of polarizable organic molecules and is consistent with the concept of formation of organic layer at the electrode surface by Tomirov *et al.*[3] The direct measurement on the adsorption is now under examination.

3) L. G. Feoktistov, A. P. Tomirov and I. G. Sevastyanova, *Electrochimiya*, **1**, 1300 (1965).

The effect of the adsorption of acrylonitrile onto the cathode surface is cosidered to appear in many aspects. The effect of reagents for the pH adjustment was mentioned already and the effect of temperature should be examined. The result is shown in Fig. 7. The yield of ADN remains to be almost constant, but the yield of propionitrile increases with the increasing temperature. This result is thought to be probable from the consideration on the adsorption equilibrium; the adsorbed amount of acrylonitrile decreases relatively with the rise in temperature. The constancy in the adiponitrile yield should be attributed to the increasing reactivity of the adsorbed acrylonitrile with temperature.

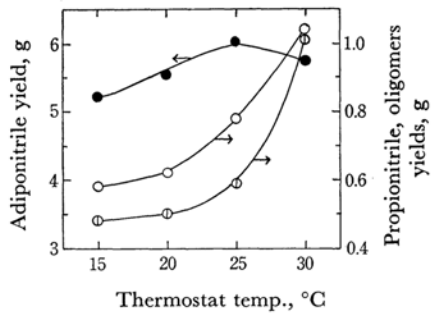

Fig. 7. Relation of yields and temperature.
○ Propionitrile, ● Adiponitrile, ◑ Oligomers

As has been discussed above, this reaction occurs through the anionic intermediates and the reactivity of those anions play an essential role in the present system and thereby the solvent effect should be anticipated. Some examinations were carried out in this respect and the result is shown in Table 3. It is clear that the higher the dielectric constants or the ionization potentials of the solvent, the less

TABLE 3. SOLVENT EFFECTS

Acrylonitrile 0.5 mol, QAS 0.1 mol, H_2O 1.0 mol, Solvent 0.5 mol, Temperature 25°C, 5 hr

Solvent	Voltage V	Electric quantity A·hr	Current density A/dm²	pH		Adiponitrile g	Adiponitrile %
1,4-Dioxane	14.0	5.04	3.36	4.7	4.6	8.05	73.3
N,*N*-Dimethylformamide	10.0	3.90	2.60	6.5	5.6	4.25	50.0
Acetonitrile	10.0	4.60	3.06	4.3	3.7	4.21	42.0
Dimethyl sulfoxide	10.0	2.82	1.88	7.5	7.7	2.29	37.3

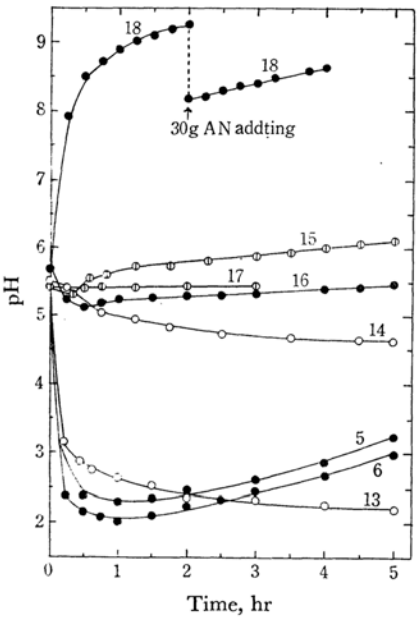

Fig. 8. Time change of pH. (Numbers in figure refer to Exp. Nos. shown in Table 1.)

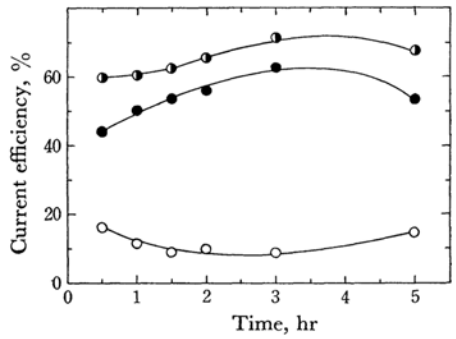

Fig. 9. Changes in current efficiencies with time.
● Adiponitrile, ○ Propionitrile,
◑ Total

the yield of adiponitrile. This shows that the extent of the solvation of ion-pairs influences the reaction. Since the free dianions react with protons more easily than the ion-pairs of the dianions and ammonium cations, this shows also that the dianions react with acrylonitrile in a near-adsorbed state at the vicinity of the cathode.

In the present experiments, the current efficiency for the production of adiponitrile does not exceed 75%. It would be considered that this is owing to the contribution of the electrolysis of QAS, for the reduction potential of QAS is close to that of acrylonitrile.

In this connection, the time change of pH and the product yields were measured and the result is shown in Figs. 8 and 9. Under normal conditions, pH of the system becomes acidic as time passes, but no remarkable changes in the yields of products were observed.