隔離槽中陰陽極組對電解丙酮縮合生成二丙烯醇之動力學

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摘　要

研究陰陽極組對電解丙酮的阿跺反應機構及動力現象，結果發現陰極室內 DAA 的生成速率較陽極室內快，而且陰陽極的反應速率與丙酮濃度皆呈一次反應，此縮合反應陰陽極的活化能分別為 45.3 及 90.0KJ/mol。

Kinetics of Aldol Condensation of Acetone to Produce Diacetone Alcohol by Paired Electrolysis in a Divided Cell

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Abstract

The mechanism and kinetics of aldol condensation of acetone by paired electrolysis were studied. The results indicate that the rate of formation of diacetone alcohol (daa) in catholyte is faster than that in anolyte. The reaction orders in both anolyte and catholyte are first order with respect to acetone. The activation energies of aldol condensation of acetone in catholyte and anolyte are 45.3 and 90.0 KJ-mole^{-1}, respectively.

1. Introduction

To produce useful and special chemicals is an interesting and important technique. Aldol condensation belongs to one of the techniques of organic synthesis. Aldol condensation was postulated to produce special chemicals using chemical reaction method which, in general, generated a lot of pollution agents as well as the catalyst which could not be regenerated. The catalysts or redox reagents can be regenerated by electrolysis [1-7]. Few or no pollutants are produced by electrolysis. Especially, the paired electrolysis for synthesis of special chemicals was reported in our previous papers [8-12]. Traditionally, only one working electrode in an electrolysis system was used. However, two working electrodes are used simultaneously in a paired electrolysis system. Theoretically, yield as well as current efficiency by paired electrolysis are higher than that of a single working electrode. The power consumption is significantly decreased by using paired electrolysis, Furthermore, in some case, high selectivity of product was obtained by paired electrolysis.

Organic electrochemistry, single or paired electrolysis, is very popular method to synthesize organic compounds. Unfortunately, few or no papers concerned aldol condensation by paired electrolysis. It is wellknown that aldol condensation of acetone is catalyzed by both proton, H^+, and OH^- anion [6,7]. Based on the reaction mechanism of both anodic and cathodic aldol condensation, the H^+ and OH^- can be simultaneously generated in situ by paired electrolysis in aqueous solution. Then acetone was catalyzed by the generted H^+ and OH^- species produced at anode and cathode, respectively. The intermediates of carbocation and carboanion were simultaneously appeared in the electrolyte. Diacetone alcohol was obtained when the intermediate reacted with the reactant again.

The factors affected the aldol condensation by paired electrolysis were reported in the previous report [14]. However, the kinetics of paired electrolysis was not mentioned. In this study, the kinetics of aldol condensation of acetone to produce diacetone alcohol by paired electrolysis in a divided cell was systematically studied.
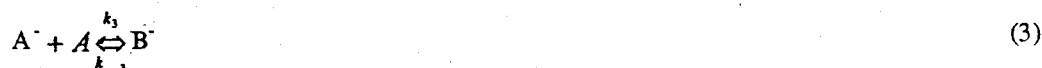
2. Experimental

The paired electrosynthesis of diacetone alcohol was performed in a divided cell using platinium plates as both anode and cathode. The anolyte and catholyte were divided by a porous glass. The electrolytes were prepared by mixing desired amounts of sodium chloride and acetone in a fixed volume of distillated water. At the beginning of a run, the temperature of the cell was controlled at a desired value by water bath. Whe the system was at steady state, a given current was supplied from the power supply (Amel-550). During a run, both catholyte and anolyte were sampled periodically and analyzed by a gas chromatography (Shimadzu GC-9A).
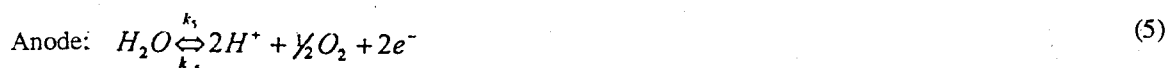
3. Results and Discussion

3.1 Reaction mechanism and rate equation

The acetone was the raw material for aldol condensation to produce diacetone alcohol in both catholyte and anolyte by paired electrolysis. Based on the paired electrolysis of water and aldol condensation of ketone, the mechanism of aldol condensation of acetone was proposed as following.

Cathode:
$$2H_2O + 2e^- \underset{k_{-1}}{\overset{k_1}{\Longleftrightarrow}} 2OH^- + H_2 \tag{1}$$

$$A + OH^- \underset{k_{-2}}{\overset{k_2}{\Longleftrightarrow}} A^- + H_2O \tag{2}$$

$$A^- + A \underset{k_{-3}}{\overset{k_3}{\Longleftrightarrow}} B^- \tag{3}$$

$$B^- + H_2O \underset{k_{-4}}{\overset{k_4}{\Longleftrightarrow}} B + OH^- \tag{4}$$

where A is acetone, A$_-$ is acetone carbanion, B$^-$ is diacetone alcohol carbanion and B is diacetone alcohol.

Anode:
$$H_2O \underset{k_{-5}}{\overset{k_5}{\Longleftrightarrow}} 2H^+ + \tfrac{1}{2}O_2 + 2e^- \tag{5}$$

$$A + H^+ \underset{k_{-6}}{\overset{k_6}{\Longleftrightarrow}} A^+ + H_2O \tag{6}$$

$$A^+ + A \underset{k_{-7}}{\overset{k_7}{\Longleftrightarrow}} B^+ \tag{7}$$

$$B^+ + H_2O \underset{K_{-8}}{\overset{K_8}{\Longleftrightarrow}} B + H^+ \tag{8}$$

where A^+ is acetone carbanium B$^-$ is diacetone alcohol carbonium. Accordingly, to the mechanism of aldol condensation of acetone in both cathodic and anodic reactions was shown in Equations (1) to (8). The formation rate of product, DAA, in catholyte was

$$R_B = k_4(B^-) - k_{-4}(B)(OH^-) \tag{9}$$

The formation rate of A$^-$ and B$^-$ were RA$^-$ and RB$^-$, respectively,

$$R_{A^-} = k_2(A)(OH^-) - k_{-2}(A^-) - k_3(A^-)(A) + k_{-3}(B^-) \tag{10}$$

$$R_{B^-} = k_3(A^-)(A) - k_{-3}(B^-) - k_4(B^-) + k_{-4}(B)(OH^-) \tag{11}$$

AT pseudo-steady state

$$R_{A^-} = 0 \tag{12}$$

$$R_{B^-} = 0 \tag{13}$$

Substituting Equation (12) into Equation(10),

$$(A^-) = \frac{k_2 (A)(OH^-) + k_{-3}(B^-)}{k_{-2} + k_{-3}(A)} \tag{14}$$

Combination of Equations (11), (13) and (14)

$$(B^-) = \frac{k_2 k_3 (A)^2 (OH^-) + k_{-4}(B)(OH^-)[k_{-2} + k_{-3}(A)]}{(k_{-3} + k_4)[k_{-2} + k_3(A)]} \tag{15}$$

Substituting Equation(15) into Equation (9), the formation rate of DAA, R_B, was

$$R_B = \frac{k_2 k_3 k_4 (A)^2 (OH^-) - k_{-3} k_{-4}(B)(OH^-)[k_{-2} + k_3(A)]}{(k_{-3} + k_4)[k_{-2} + k_3(A)]} \tag{16}$$

At initial state, $(B) = 0$, and Equation (16) can be simplified,

$$R_B = \frac{k_2 k_3 k_4 (A)^2 (OH^-)}{(k_{-3} + k_4)[k_{-2} + k_3(A)]} \tag{17}$$

At high concentration of acetone, $k_3(A) >> k_{-2}$,

$$R_B = k'(A)(OH^-) \tag{18}$$

After a constant amount of electricity passed, (OH^-) is constant, then

$$R_B = k''(A) \tag{19}$$

where k'' is $k(OH^-)$.

Similarly, a rate equation can be obtained in anolyte.

$$R_B = k''(A) \tag{20}$$

3.2 Effect of amount of electricity passed on pH

Fig.1 shows pH values vs. amount of electricity passed. The pH values in both catholyte and anolyte changed from 7 to 12 and 7 to 3, respectively, during about 60 coulumbs electricity passed. At a fixed applied potential, the electrochemical reactions are not rate determining steps as shown in Equations (1) and (5), so it does not affect the rate expressions such as Equations (19) and (20). Otherwise, the catalysts H^+ and OH^- was disappeared by reacting with acetone and was reproduced by producing procedure each other as shown in Equations (2), (6) and Equations (4), (8). So the pH values both in anolyte and catholyte are constant during about 60 coulumbs electricity passed.

3.3 Effect of current density on yield

Fig.2 shown that the yield of DAA is 780g/F and is independent of the current density. The result also describes that the electrochemical reaction is not rate determining step either.

3.4 Effect of concentration of acetone on reaction rate

The formation rates of DAA in both catholyte and anolyte increased from 3.5 to 17 M-hr^{-1} and 2 to 7.5 M-hr^{-1}, respectively, by increasing the concentration of acetone from 2 to 8 M as shown in

Figs.3 and 4. The experimental results of the reaction order with respect to acetone in both anolyte and catholyte are 0.99 and 1.1, respectively, i.e. first order.

3.5 Effect of temperature on reaction rate

Figs.5 and 6 show the activation energies of aldol condensation of acetone in both catholyte and anolyte by paired electrolysis are 45.3 and 90.0 KJ-mole^{-1}, respectively. Accordingly, the reaction rate in catholyte is faster than that in anolyte by paired electrolysis. By using H^+ and OH^- as catalysts, the activation energies of aldol condensation were 67.3 and 70.6 KJ-mole^{-1}, respectively, which were reported in a heterogeneous catalyst system [13].

3.6 Energy consumption of paired electrolysis

The energy consumption could be decreased by appling the interrupt electrolysis. The energy consumption by using single anode as working electrode was higher than that of catholyte only. However, the energy consumption of paired electrolysis was the smallest one and was in the range from 0.054 to 0.024 kW · h/mole DAA in this system. Increasing the reaction time from 1 to 4 hrs the power consumption decreases from 0.054 to 0.026 kW · h/mole DAA. Further lasting the reaction time to 5 hrs, the power consumption reaches to 0.024 kW · h/mole DAA.

3.7 Comparison of experimental results and the theoretical analysis

By comparing Equation (21) with Equation (20), and Equation (22) with Equation (19), the results indicated that the experimental results correlated with the theoretical analysis ones well. Both the experimental results and the theoretical analysis showed that the reaction order of acetone was first order in both anolyte and catholyte.

Conclusions

Aldol condensation of acetone by paired electrolysis in a divided cell was obtained. The reaction rate in catholyte is faster than that in anolyte. The reaction order in both catholyte and anolyte are first order with respect to acetone. The activation energies in both catholyte and anolyte are 45.3 and 90.0 kJ-mole^{-1}, respectively. The experimental results correlated with the theoretical analysis ones well, i.e.

Anolyte: $R_B = k_1(A)^{1.1}$ (21)

Catholyte: $R_B = k_2(A)^{0.99}$ (22)

Acknowledge

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Table 1 Energy consumption of paired electrolysis

Cathode: Pt   Anode: Pt   Electricity: 120 coul   Electrolyte: 2M
Temperature: 25°C   Current density: 25 mA-cm^{-2} Acetone: 2M

Time,hr	Engery Consumption, kw-hr/mole daa		
	Catholyte	Anolyte	Paired
1	0.072	0.220	0.054
2	0.057	0.119	0.039
3	0.048	0.093	0.032
4	0.043	0.065	0.026
5	0.041	0.057	0.024

Table 2 Comparison of experimental results and the theoretical analysis.

Acetone	Reaction order	
	Theoretical	Experimental
Catholyte	1.0	0.99
Anolyte	1.0	1.1
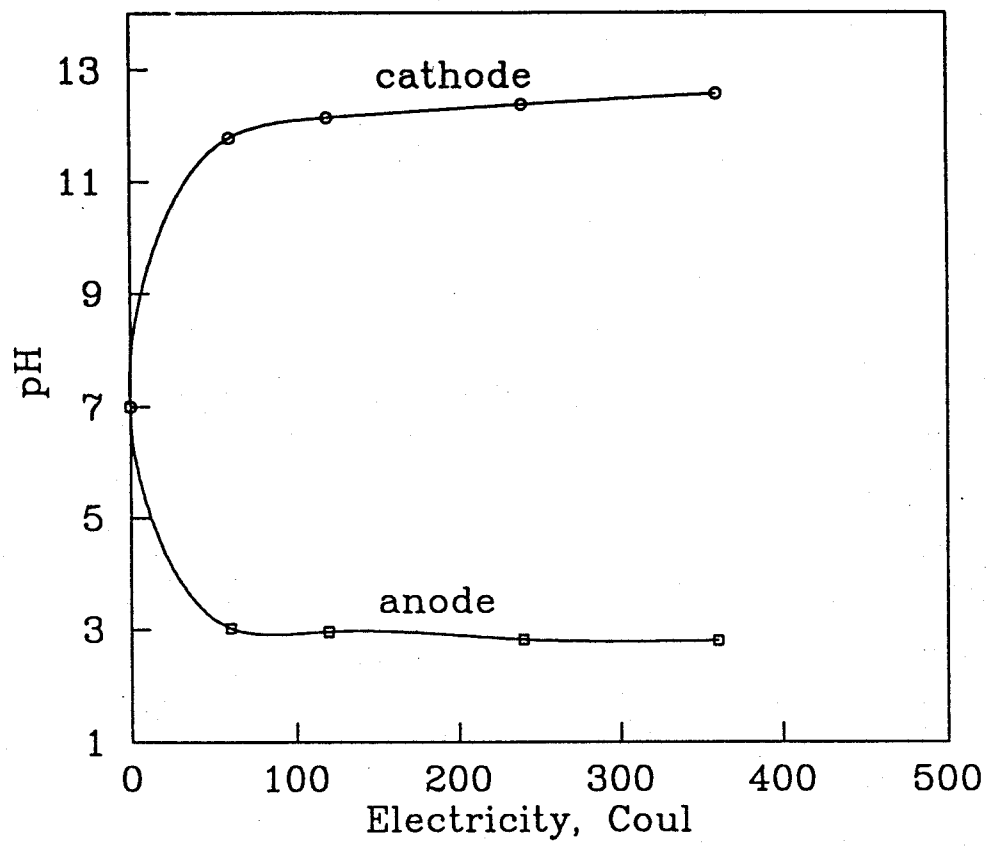
Fig.1 Plot of pH vs. time in a divided cell by paired electrolysis. Electrolyte: 2M NaCl Temperature: 25°C Acetone: 2M Electrode: Pt Current density: 25 mA-cm^{-2}.
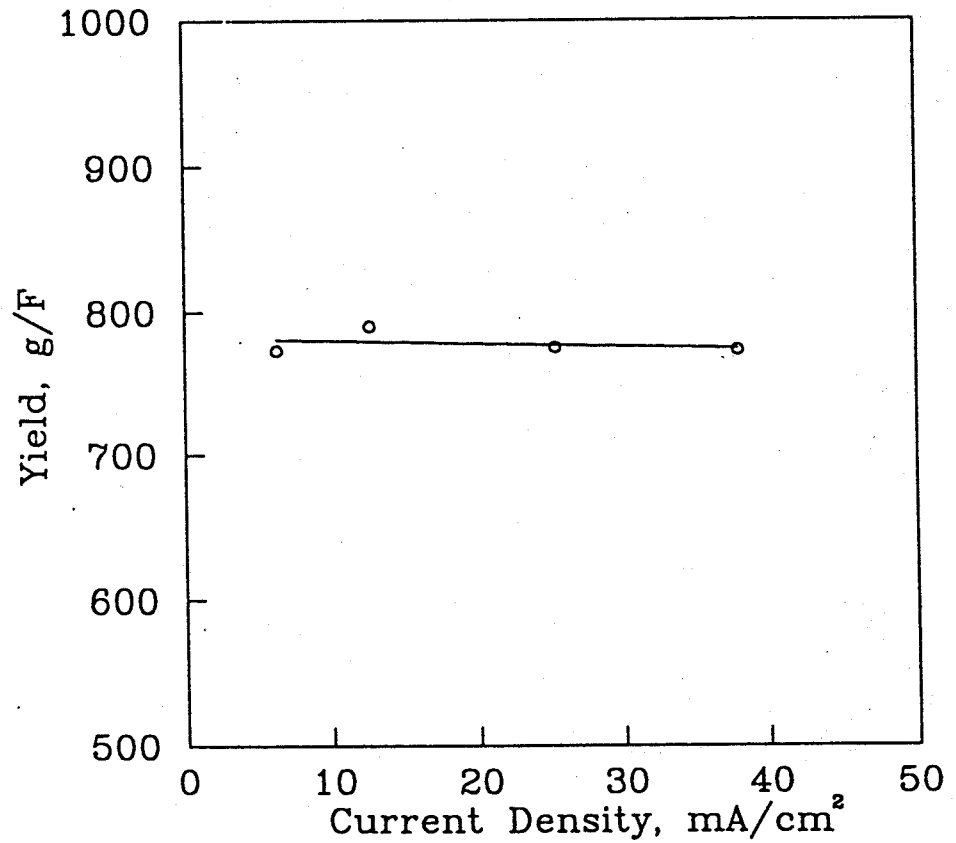

Fig.2 Effect of current density on the yield of paired electrolysis. Cathode: Pt Anode: Pt Electrolyte: 2M NaCl Electricity: 120 coul Acetone: 8M Temperature:25°C
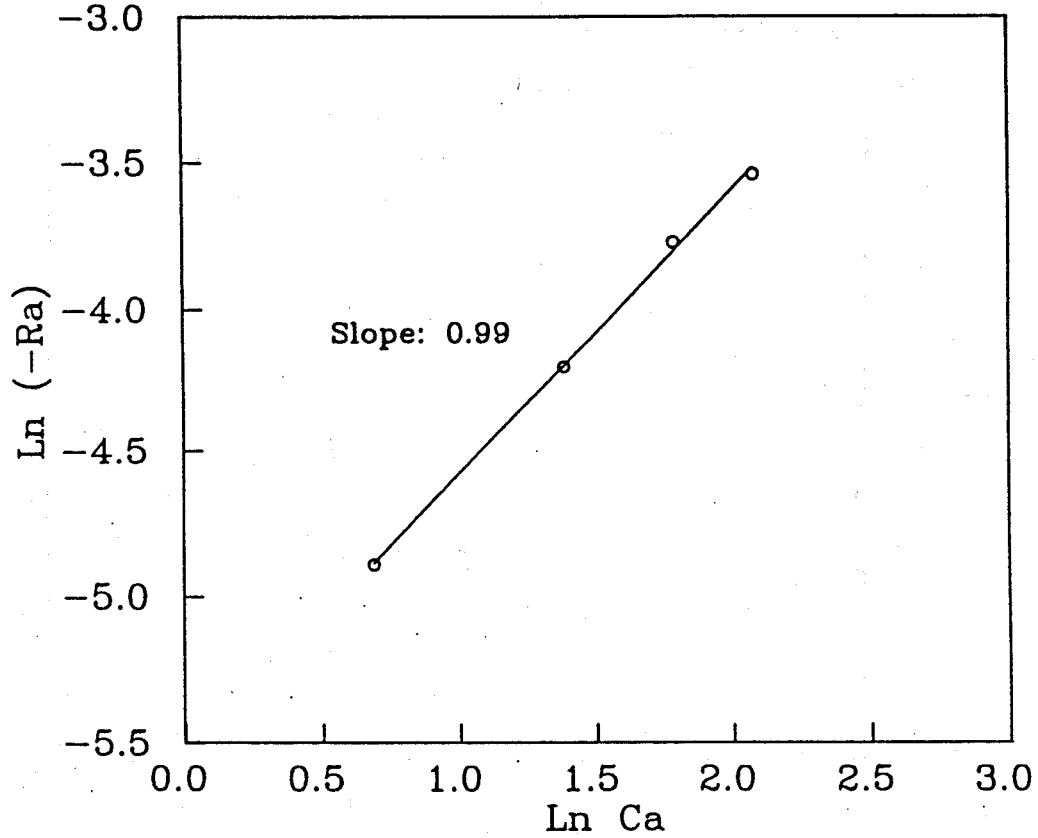
Fig.3 Effect of concentration of acetone on reaction rate in catholyte Cathode: Pt Anode: Pt Electricity: 120 coul Electrolyte: 2M NaCl Current density: 25 mA-cm^{-2} Temperature: 25℃
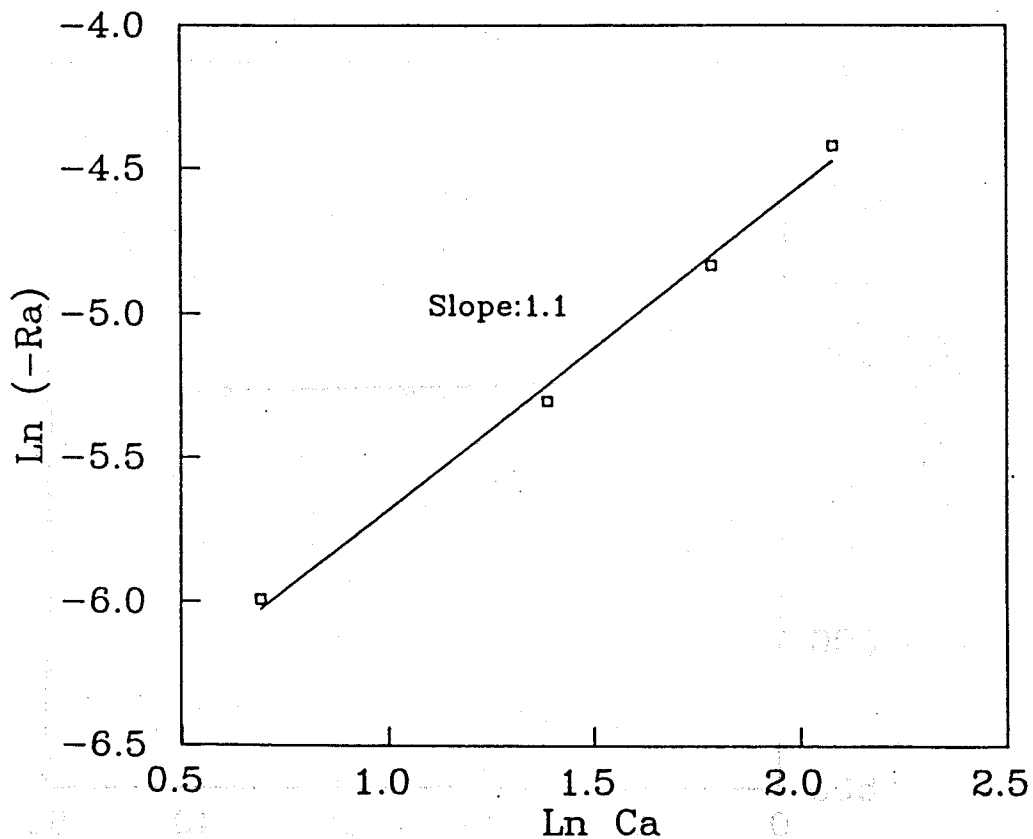

Fig.4 Effect of concentration of acetone on reaction rate in anolyte. Cathode: Pt Anode: Pt Electricity: 120 coul Electrolyte: 2M NaCl Current density: 25 mA-cm^{-2} Temperature: 25℃
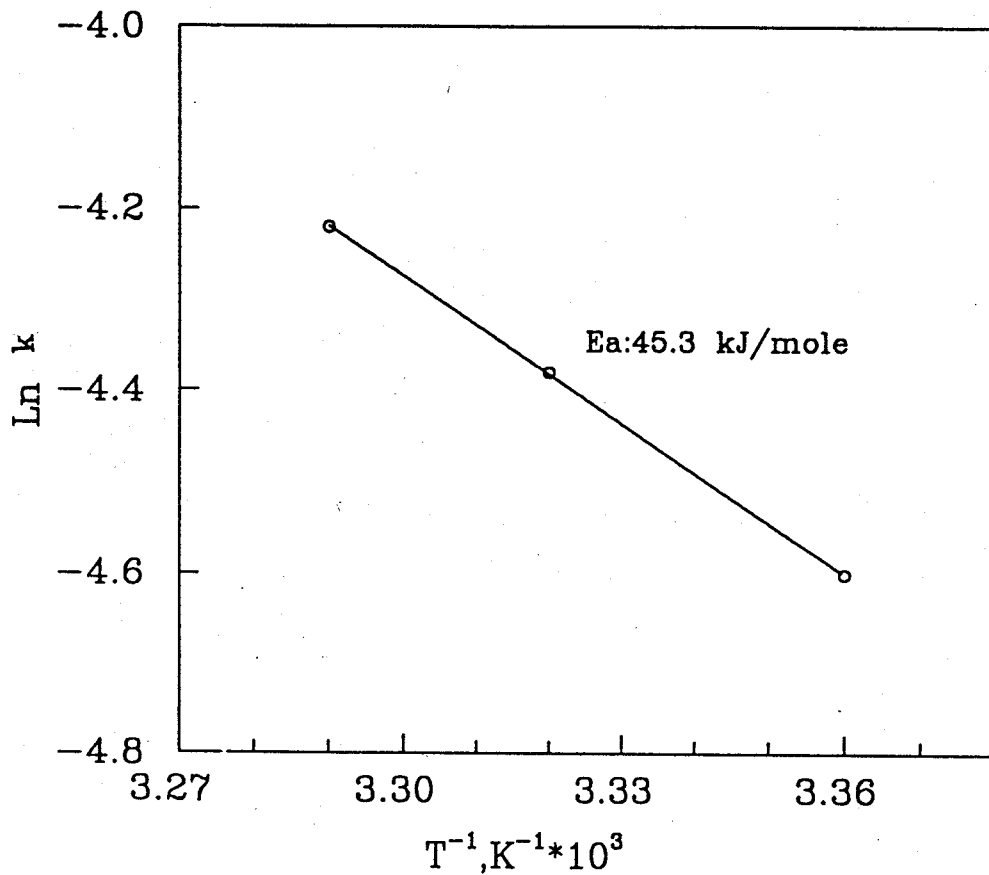
Fig.5 The Arrhenius plot of DAA in catholyte. Cathode:Pt Anode:Pt Current density: 25 mA-cm^{-2} Acetone: 2M Electrolyte:2M NalCl
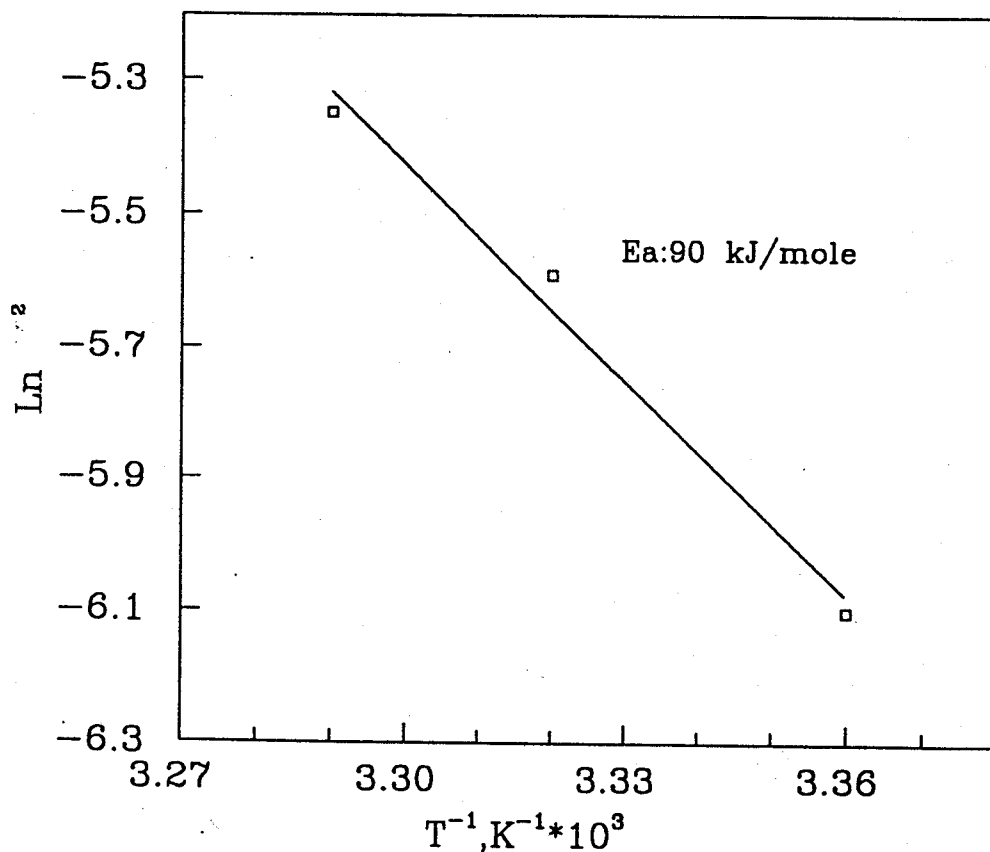

Fig.6 The Arrhenius plot of DAA in anolyte. Cathode: Pt Anode: Pt Current density: 25 mA-cm^{-2} Acetone: 2M Electrolyte: 2M NaCl