

Reduction of Salicylic Acid to Salicylaldehyde with Modulated Alternating Voltage

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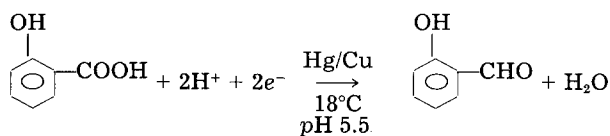
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ABSTRACT

The effect of superimposing sinusoidal, triangular, and square-wave alternating voltage (aV) on the potentiostatic reduction of salicylic acid to salicylaldehyde has been studied. Polarization curves with aV modulation were measured with an amalgamated copper rotating disk electrode. Enhanced dc current densities were observed with increasing magnitude of superimposed aV. However, aV frequency and type did not have significant effect on the resulting dc current densities. Batch cell electrolysis experiments were conducted with a H-type cell. The conversion of salicylic acid and yield of salicylaldehyde were measured as functions of electrolysis time, aV magnitude, type, and frequency. The superimposed aV significantly enhanced the reaction rate, conversion of salicylic acid, and the yield of salicylaldehyde. The energy consumption of ac electrolysis was higher than that of dc electrolysis.

In recent years, alternating current (ac) electrolysis has been used as a technique to enhance the rate of organic electrochemical reactions. Two methods may be employed in the ac electrolysis. The first method is a galvanostatic alternating current modulation technique, in which a constant alternating current component is superimposed onto a direct current (dc) component, and the resulting composite current is applied to the electrochemical cell. The second method is a potentiostatic alternating voltage (aV) modulation technique, in which the electrolysis is carried out by controlling the potential of the working electrode, with respect to a reference electrode at a constant direct potential (dc), superimposed with an alternating voltage component. Chin and Cheng (1) conducted an experimental study on the electro-oxidation of phenol, and found that ac and aV strongly modified the shape of the polarization curves. Their batch cell experiments showed an increase in the conversion of phenol with increasing aV magnitude and decreasing aV frequency. Alkire and Tsai (2) investigated the electrosynthesis of propylene oxide from a propylene saturated bromide solution with ac. They found that the current efficiency decreased with increasing ac frequencies. Fedkiw and Chao (3) studied the reduction of nitrobenzene, using square wave pulsating currents, and reported an increased yield and selectivity of p-aminophenol with ac electrolysis.

This paper is concerned with a study of the effect of aV modulation on the reduction of salicylic acid to salicylaldehyde on an amalgamated copper electrode. Salicylaldehyde is manufactured as an intermediate in the synthesis of coumarin, perfumes, and other flavoring materials. It is also used as electroplating and agricultural chemicals. Salicylaldehyde is produced by electrolytically reducing salicylic acid on a mercury electrode



[1]

The process has many difficulties. In aqueous solutions, the reduction reaction usually proceeds with a simultaneous hydrogen evolution reaction. The aldehyde may be further reduced to the alcohol, if the electrolysis condition is not carefully controlled (4). In dc electrolysis, the yield of salicylaldehyde is about 30-50% (5).

In the present work, the method of aV modulation is used to carry out the electroreduction of salicylic acid to salicylaldehyde. This paper describes the results on: (i) the dc current vs. dc potential relations, for the reduction of salicylic acid under the superimposed aV conditions; and (ii) the effect of aV on the conversion of salicylic

acid, the yield of salicylaldehyde, and the energy consumption of a potentiostatic batch electrolysis.

Experimental

Experimental setup and instrumentation.—A three compartment H-type glass cell (The Electrosynthesis Company Incorporated, Model C-200) was used in the present investigation. Amalgamated copper served as the working electrode. A saturated calomel electrode served as the reference electrode, and a platinum screen was used as the counterelectrode. Provisions were made to insert a pH electrode and a thermometer into the working electrode compartment, to monitor the pH and electrolyte temperature. A sampling port was also provided on the cell cover to withdraw samples of the catholyte for chemical analysis. The entire cell assembly was immersed in a constant temperature water bath.

The electrolyte in the cathodic compartment was an aqueous solution of 0.1M salicylic acid, 0.75M boric acid, 0.1M sodium sulfite, and 10% (by weight) sodium sulfate. A 10% sodium sulfate aqueous solution was used as the anolyte. The pH of the catholyte was 5.5, and was maintained at this value during the experiments by the addition of small amounts of dilute sulfuric acid or sodium hydroxide. Close control of pH was necessary to stabilize an aldehyde complex with sodium sulfite and boric acid, and to prevent further reduction of the aldehyde. The amount of sulfuric acid or sodium hydroxide added into the cell was so small that its effect on the electrolyte concentration was negligible. The cell temperature was maintained at $18^\circ \pm 2^\circ\text{C}$ throughout this study.

Figure 1 shows the electrical circuit diagram. A potentiostat (Wenking, HP 72) was used to control the dc potential level. A function generator, (Hewlett Packard 3311A) connected across a variable resistor R_1 , was used to superimpose sinusoidal, triangular, and square-wave aV, onto the dc potential. A microcomputer (Commodore PET 4032) interfaced with a digital data acquisition unit (Hewlett Packard 3421A) was used to monitor the dc electrode potential, dc current, root-mean-square (rms) ac current, dc cell voltage, and rms ac cell voltage.

Polarization measurements.—An amalgamated copper rotating disk electrode, having an exposed area of 0.505 cm^2 , was used to determine the dc current vs. dc potential relation, for the reduction of salicylic acid under the superimposed aV conditions. The procedure involved the polishing of a copper rotating disk electrode to 600 mesh smoothness, and amalgamating the copper surface by treating it with dilute nitric acid and mercury. The electrode was electrolytically cleaned in dilute sulfuric acid before being transferred into the test cell. The working electrode was then set at a desired rotational speed and the open-circuit electrode potential (vs. SCE) was noted. A constant aV of known waveform, magnitude, and frequency was applied to the cell through the potentiostat. The dc potential was then increased step-

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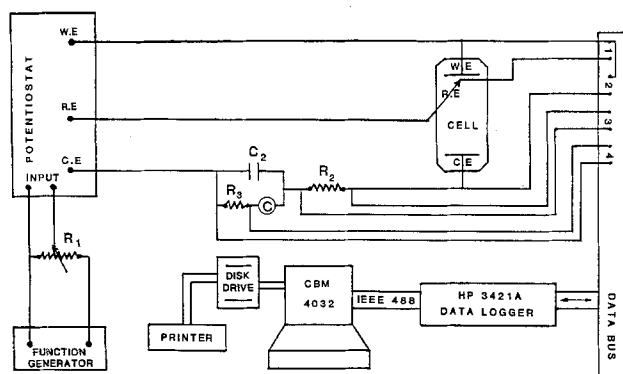


Fig. 1. Electrical circuit diagram for ac electrolysis

wise from -2.0V to 0V vs. SCE, at a step rate of 100 mV per minute. The resulting dc current was measured as a function of dc potentials. The polarization measurements were performed over a range of rotational speeds, from 600 to 2000 rpm . The superimposed aV varied from 0 to 1.0V rms; the aV frequency ranged from 20 to 2000 Hz ; and the types of aV waveform used were sinusoidal, triangular, and square waves.

Potentiostatic electrolysis with a batch cell.—For the batch cell electrolysis experiments, the electrochemical cell was assembled in the same manner as described for the polarization studies. However, the working electrode was a stationary amalgamated Cu sheet, $5 \times 3 \times 0.04\text{ cm}$. The cell solution was stirred with a magnetic stirrer at a constant rate. The electrodes were connected to the electrical circuit, and the open-circuit electrode potential was noted. Power was then switched on. The dc electrode potential was set at a desired level, and an aV of known waveform, magnitude, and frequency was superimposed onto the dc potential. The electrolysis was carried out for 3 h and the computer aided data acquisition unit was used to record the dc electrode potential, dc current, root-mean-square (rms) ac current; dc cell voltage, and rms ac cell voltage. As the electrolysis proceeded, the pH of the catholyte tended to increase, and was adjusted to 5.5 ± 0.1 by adding dilute sulfuric acid to the cell. A 5 ml sample of catholyte was withdrawn from the cell every 45 min for the chemical analysis of salicylic acid and salicylaldehyde, using the high performance liquid chromatography (HPLC) technique. The sample was extracted twice with 10 ml of ether and the resulting ether solution was diluted to 50 ml with methanol. The HPLC unit consisted of a chromatography pump (Waters Associates, Model 6000A), a μ -Bondapak C_{18} (containing bound $\text{Si}(\text{CH}_2)_{17}\text{CH}_3$ groups) reverse phase column, and a UV absorbance (254 nm) detector (Waters Associates, Model 440). A 25% methanol solution in distilled water

was used as the solvent, and the flow rate was fixed at 1.5 ml/min . The salicylic acid and salicylaldehyde peaks were well separated and the maximum error of the chemical analysis was $\pm 10\%$.

The batch cell electrolysis experiments were conducted over a range of dc potentials from -1.75V to -2.2V vs. SCE, aV magnitude from 0 to 750 mV rms, and aV frequency from 20 to 400 Hz . The experiments were carried out with sinusoidal, symmetrical triangular, and square wave aV.

Results and Discussion

Polarization measurements.—Figure 2 shows the effect of aV magnitude on the cathodic current-potential relation obtained with 60 Hz sinusoidal aV at 2000 rpm , $\text{pH } 5.5$, and at 18°C . Two plateaus were observed on the polarization curve, without any superimposed aV (solid line). The first current wave was due to the reduction of salicylic acid to salicylaldehyde. The second current wave, beginning approximately at -1.2V vs. SCE, was due to the reduction of SO_3^{2-} ions in the supporting electrolyte to $\text{S}_2\text{O}_4^{2-}$ ions (6). The polarization curves with superimposed aV, varying from 250 mV to 1000 mV (rms) are given as the dashed lines. Superimposition of aV enhanced the dc current densities for the reduction of salicylic acid and suppressed the reduction reaction of the SO_3^{2-} ion, because the second current wave disappeared on the polarization curves with superimposed aV. The enhancement in dc current increased as the magnitude of aV did. With 1000 mV rms aV, the dc current density was approximately one order of magnitude higher than that without aV. This increase in the rate of reduction of salicylic acid can be attributed to the ability of aV to behave as a depolarizer, which reduced the overpotentials and enhanced the apparent electrokinetics (1). Superimposed aV also shifted the rest potential of the electrolytic system. The rest potentials measured with superimposed aV were more positive than that without superimposed aV.

Figure 3 shows the polarization curves with different frequencies (20 – 2000 Hz) of a sinusoidal aV at 500 mV (rms). For comparison, the polarization curve obtained with dc alone is shown as the solid line. The frequency of superimposed aV did not have a significant effect on the dc current vs. dc potential behavior, for the reduction of salicylic acid on amalgamated copper electrode. The current-potential measurements were also made with symmetrical triangular and square wave aV at 500 mV (rms) magnitude and 60 Hz frequency. It was found that the aV waveform did not have any significant effect on the dc current densities and the rest potential changes.

Batch cell electrolysis.—Figure 4 shows the effect of aV magnitude on the dc current density of a batch electrolysis cell as a function of time, when the cell was superim-

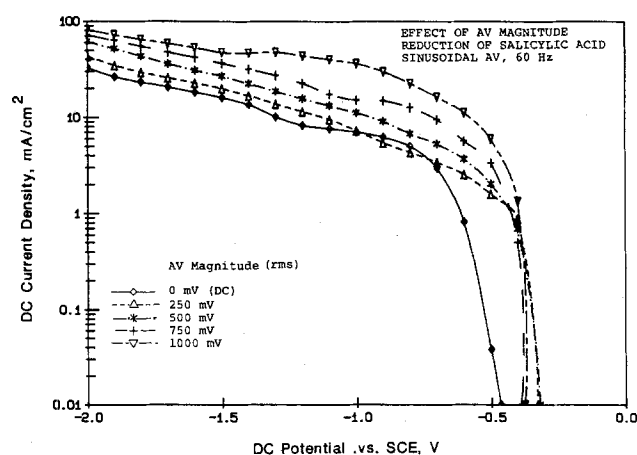


Fig. 2. DC current vs. dc potential curves for the reduction of salicylic acid when the electrode was superimposed with 60 Hz sinusoidal aV ranging from 0 – 1000 mV rms. An amalgamated copper rotating disk electrode at 2000 rpm was used for the measurement.

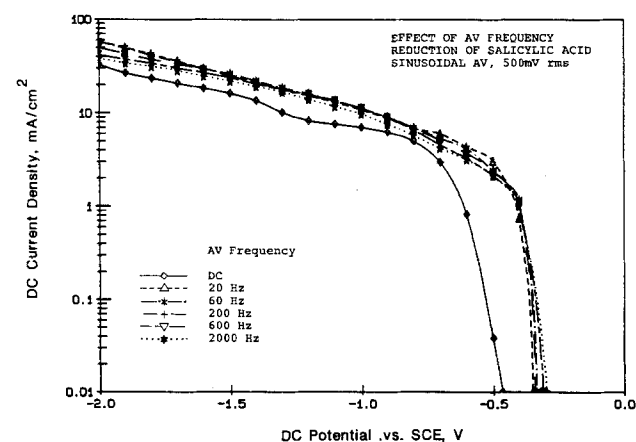


Fig. 3. Effect of aV frequency on the dc current vs. dc potential curves for the reduction of salicylic acid on an amalgamated copper rotating disk electrode. The electrode was superimposed with sinusoidal aV at 500 mV rms (20 – 2000 Hz), and the measurements were carried out at 2000 rpm .

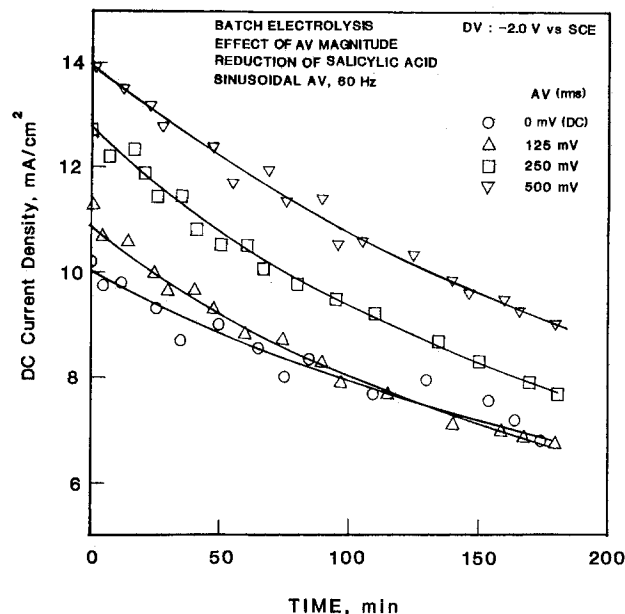


Fig. 4. DC cell current density, as a function of time, for a potentiostatic batch electrolysis of the reduction of salicylic acid to salicylaldehyde on an amalgamated copper electrode. The electrode potential was controlled at $-2.0V$ vs. SCE and was superimposed with 60 Hz sinusoidal aV varying from 0 to 500 mV rms.

posed with 60 Hz sinusoidal aV. In these runs, the dc potential of the working electrode was set at $-2.0V$ vs. SCE and the superimposed aV varied from 0 to 500 mV rms. Similar to the polarization results, the dc current density for the reduction of salicylic acid increased as the magnitude of the superimposed aV did. The dc current density decreased with time, due to the decrease in the concentration of salicylic acid as the electrolysis proceeded. The concentrations of salicylic acid and salicylaldehyde during the electrolysis are shown in Fig. 5. For a given electrolysis time, the concentration of salicylic acid with aV modulation was lower than that of the dc electrolysis. The rate of decrease in the concentration of

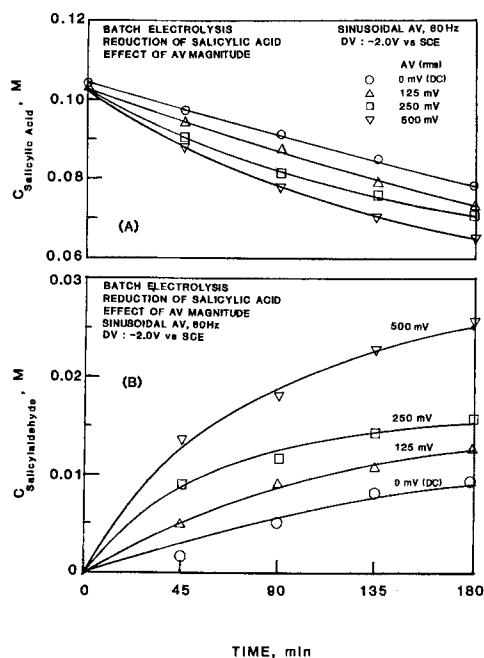


Fig. 5. Concentrations of salicylic acid (a) and salicylaldehyde (b), as functions of time, during a potentiostatic batch electrolysis for the reduction of salicylic acid to salicylaldehyde on an amalgamated copper electrode. The electrode potential was controlled at $-2.0V$ vs. SCE and was superimposed with 60 Hz sinusoidal aV, ranging from 0-500 mV rms.

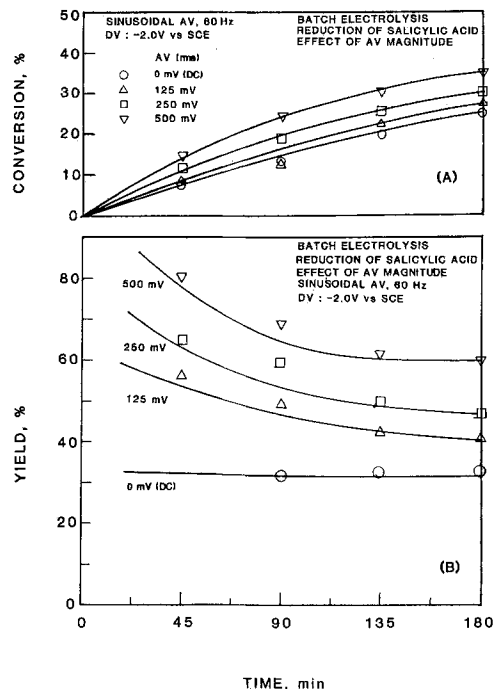


Fig. 6. Conversion of salicylic acid (a) and yield of salicylaldehyde (b), as functions of electrolysis time, when the potential of an amalgamated copper electrode was controlled at $-2.0V$ vs. SCE, and was superimposed with sinusoidal aV ranging from 0-500 mV rms.

salicylic acid increased as the magnitudes of aV did. The results indicate that the applied aV increased the reaction rate for the reduction of salicylic acid. Figure 5b shows the salicylaldehyde concentrations as a function of time. As electrolysis proceeds, the salicylaldehyde concentration in the cell increases. For any given time, the concentration of salicylaldehyde with the ac electrolysis was higher than that in the dc electrolysis. At the end of a 90 min electrolysis, with 500 mV rms sinusoidal aV, the concentration of salicylaldehyde was four times the concentration obtained without superimposed aV. The concentration of salicylaldehyde increased as aV magnitude did. The results indicate that aV modified the selectivity and enhanced the yield of salicylaldehyde.

The conversion of salicylic acid, X , is defined as

$$X = \frac{C_{\text{acid},i} - C_{\text{acid}}(t)}{C_{\text{acid},i}} \quad [2]$$

where $C_{\text{acid},i}$ is the initial concentration of salicylic acid and $C_{\text{acid}}(t)$ is the concentration of salicylic acid at the time t . The chemical yield of salicylaldehyde, Y , is defined as

$$Y = \frac{C_{\text{ald}}(t)}{C_{\text{acid},i} - C_{\text{acid}}(t)} \quad [3]$$

where $C_{\text{ald}}(t)$ is the concentration of salicylaldehyde at the time t . Using Eq. [2] and [3] and the results of chemical analysis for the concentrations of salicylic acid and salicylaldehyde, the conversion of salicylic acid and the yield of salicylaldehyde were computed. Figure 6 presents the conversion and yield data for when the cell was operated with 60 Hz sinusoidal aV, ranging from 0-500 mV rms at a dc electrode potential of $-2.0V$ vs. SCE. The conversion of salicylic acid increased with increasing aV (Fig. 6a). The slopes of the curve decreased with increasing time because of the loss of current efficiency. The chemical yield of salicylaldehyde in dc electrolysis was only 30% and was increased to 70% by modulation with 500 mV rms aV (Fig. 6b). The yield increased as the aV magnitude did, and decreased with the time. Figure 7 shows the conversion and yield obtained at the dc electrode potential of $-1.75V$ vs. SCE and with 60 Hz sinusoidal aV, ranging from 0-750 mV rms. In these runs, only a trace amount of salicylaldehyde was obtained with the

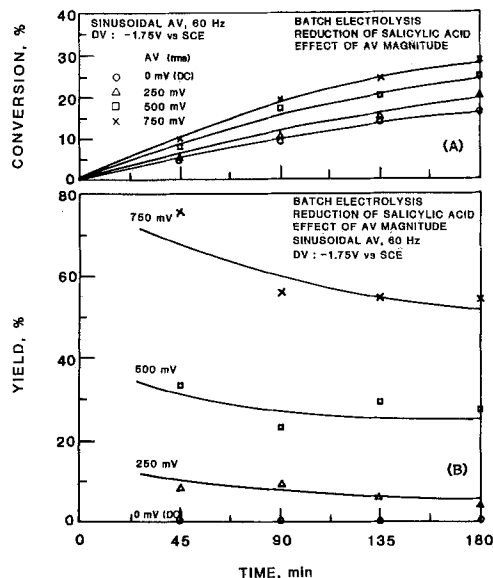


Fig. 7. Conversion of salicylic acid (a) and yield of salicylaldehyde (b), as functions of electrolysis time, when the potential of an amalgamated copper electrode was controlled at $-1.75V$ vs. SCE, and was superimposed with sinusoidal aV ranging from 0-750 mV rms.

dc electrolysis; whereas the yields increased to 60% with 750 mV rms aV. A similar experiment was also conducted at the dc electrode potential of $-2.2V$ vs. SCE. It was found that the yield of salicylaldehyde decreased at high dc potentials. The low yields of salicylaldehyde in dc electrolysis can be attributed to secondary parasitic reactions of salicylic acid and salicylaldehyde. Some of the possible secondary reactions include: electrochemical reduction of salicylaldehyde to salicyl alcohol (5), acetal formation by a chemical reaction between salicylaldehyde and salicyl alcohol, ester formation by a chemical reaction between salicyl alcohol and salicylic acid (7), one electron reduction of the $-COOH$ group in salicylic acid with a subsequent dimerization of the reduction product (8), and other unidentified reduction products and tar formation (6). Since the primary interest of this work was to study the synthesis of salicylaldehyde, no attempt was made to examine the secondary reactions and intermediate products.

The total energy consumption, W_{total} , in the ac electrolysis is given by

$$W_{total} = \int_0^t [E(t)\bar{I}(t) + \bar{E}_{rms}(t) \cdot \bar{I}_{rms}(t)] dt \quad [4]$$

where \bar{I} and \bar{I}_{rms} are the total dc cell current and the root-mean-square of the ac cell current, respectively; \bar{E} is the dc cell voltage, and \bar{E}_{rms} is the rms ac cell voltage. The total energy consumed per mole of salicylaldehyde formed may be computed as

$$\epsilon_{\text{salicylaldehyde}} = \frac{W_{total}}{\text{moles of salicylaldehyde formed}} \quad [5]$$

Normalizing the energy consumed in the ac electrolysis with the energy consumed in the dc electrolysis, a dimensionless energy consumption is defined as

$$\epsilon^* = \frac{\epsilon_{\text{ac Electrolysis}}}{\epsilon_{\text{dc Electrolysis}}} \quad [6]$$

Figure 8 shows the dimensionless energy consumption (as given by Eq. [6]) based on the yield of salicylaldehyde when the cell was superimposed with 60 Hz sinusoidal aV varying from 0 to 500 mV rms. The dc electrode potential was set at $-2.0V$ vs. SCE. With low aV of 125 mV rms or less, the enhanced yields of salicylaldehyde resulted in the energy requirements being less than that in dc electrolysis. However, with increasing magnitude of

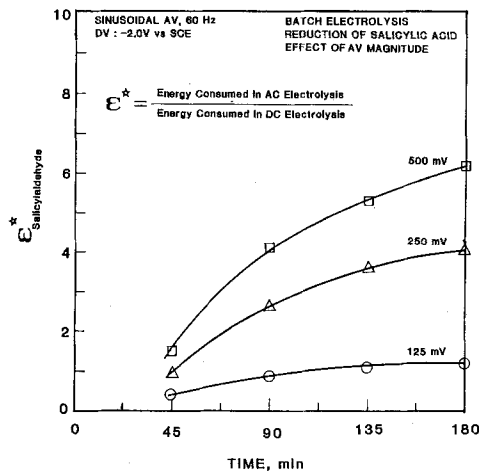


Fig. 8. Dimensionless energy consumption for a set of potentiostatic batch electrolyses, when the potential of an amalgamated copper electrode was set at $-2.0V$ vs. SCE superimposed with sinusoidal aV, ranging from 125-500 mV rms.

superimposed aV, the energy consumption in the ac electrolysis became higher than that of the dc electrolysis. The energy consumption increased with increasing aV magnitude. This was due to the fact that a large amount of the energy was consumed by the ac cell voltage and ac cell current during the electrolysis.

The batch cell experiments were also conducted to investigate the effect of aV frequency and aV waveforms. The results showed that aV frequency and aV waveforms did not have a significant effect on the conversion of salicylic acid and the yield of salicylaldehyde. The trend was similar to that observed in the polarization measurements.

Conclusions

An experimental investigation has been made of the effect of aV on the potentiostatic reduction of salicylic acid to salicylaldehyde. It was found that superimposed aV modified the dc current vs. dc potential relation for the reduction of salicylic acid on an amalgamated copper electrode. aV enhanced the dc current density, and shifted the apparent rest potential toward the positive direction. aV increased the rate of conversion of salicylic acid and improved the selectivity for the production of salicylaldehyde. The yields of salicylaldehyde increased from 30% to 80% with the superimposition of aV. The energy consumption in the ac electrolysis was higher than that in the dc electrolysis.

Acknowledgments

Acknowledgment is made to the donors of Petroleum Research Fund (Grant 14330-AC5-C), administered by the American Chemical Society, for support of this research. The authors also wish to thank Professor D. R. Rosenthal of the Department of Chemistry at Clarkson University for his assistance in chemical analysis.

Manuscript submitted Sept. 8, 1986; revised manuscript received March 3, 1987.

The Petroleum Research Fund of the American Chemical Society assisted in meeting the publication costs of this article.

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