Ultrasonic Effects on Electroorganic Processes.[1] Cavitation Threshold Values of Ultrasound-oscillating Power

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Cavitation threshold values of ultrasound-oscillating power were clearly indicated in both the electroreduction of p-methylbenzaldehyde and the elelctrooxidation of hydroquinone.

Chemical application of ultrasounds has received much attention so far.[2-7] However, the application to electrochemistry, particularly to electroorganic processes, has been relatively limited.[8-10]

From the above point of view, we have aimed to explore clear effects of ultrasounds on a variety of electroorganic processes. In our pervious work,[11-14] significant effects of ultrasounds on current efficiency and product selectivity could be found in the electroreduction of organic compounds. It was hypothesized that the product-selectivity control is rationalized as due to remarkable promotion of mass transport across the electrode interface caused by peculiar agitaiton or cavitation effect of ultrasounds. However, a question has been remained open: What kind of ultrasonic phenomenon does the promotion cause? Futhermore, it has not been made clear whether the cavitaion is exclusively required for the mass transport promotion in electrochemical reactions. Klima *et al.,*[15] Compton *et al.,*[16] and others[10] suggested influence of the cavitaion on the mass transport in electrochemical processes. Contrary, Ley and Low[17] described that the mass transport promotion is independent of the cavitaion and is rationalized as due to "acoustic streaming."

The above problem should be essentially solved by examining the influence of ultrasonic power on the ultrasonic effects. However, the influence of ultrasonic power has been very rarely reported so far.[18]

In this work, a cavitaion meter developed recently for monitoring the abilily of a variety of practical ultrasonic instruments was used to clarify quantitatively the cavitaion effect on electrooganic processes. The cavitation meter with a microphone detects sounds generated when cavities crush and indicates the total acoustic energy as "cavitation intensity index" without physical unit.

In order to determine the ultrasonic effects, the electro-reduction and -oxidation of p-methylbenzaldhyde and hydroquinone were used as typical models for electroorganic processes (Scheme 1) well-known to be mechanistically deffusion-controlled.[14,18,19]

An H-shaped divided cell equipped with a lead disc cathode (Diameter, 3.3 cm) and a platinum counter electrode (3 x 4 cm) was used for galvanostatic electrolysis of p-methylbenzaldehyde (40 mM) at 20 $mAcm^{-2}$ in a 0.25 M H_2SO_4 / 50% CH_3OH catholyte (100 cm^3). A stepped horn (A titanium lod with 1.9 cm diameter) connected with a PZT oscillator (20 kHz) and a microphone of cavitation meter (Arock Industrial Co., Ltd., Model KS-8201R) were inserted into the working-electrode chamber. The working electrode surface was positioned perpendicularly to the propagating direction of ultrasonic wave, 2.5cm apart from tip of the horn. For steady state voltammetry, a small lead plate cathode (1 x 1 cm) was used. Voltammograms for the oxidation of hydroquinone (20 mM) were measured on a platinum plate (1 x 1 cm) in a 0.1 M CH_3COONa-0.1 M CH_3COOH / 50% DMF. The reduction products (HD and HM in Scheme 1) were analyzed by HPLC.

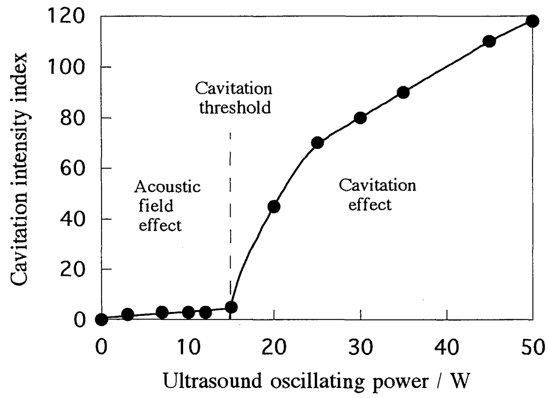
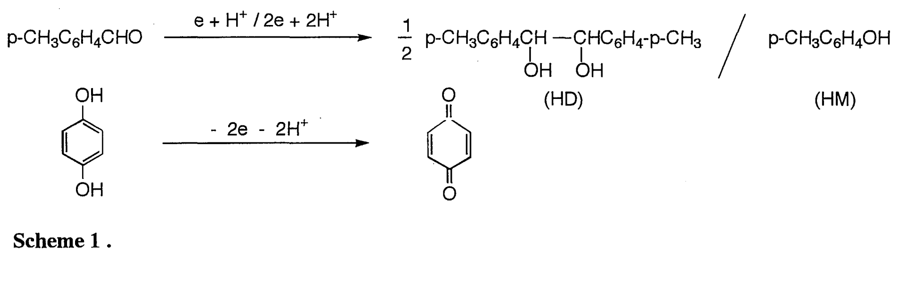


Figure 1. Relationship between cavitation intensity index and ultrasound oscillating power without current in a catholyte for the reduction of p-methylbenzaldehyde.

Figure 1 shows a relationship between cavitation intensity index monitored by the cavitation meter and ultrasound oscillating power in the cathodic solution for the reduction of p-methylbanzaldehyde. The index increases gradually at < 15 W and steeply at > 15 W with increase in the power. It is easily



Scheme 1 .

understood that the ultrasonic cavitation in the solution can take place at > 15 W while only the vibration of the solution at < 15 W. The power of 15 W is a so-called cavitation threshold value and generally should depend on the whole geometry of apparatus and the nature of solution. It is likely that acoustic field and cavitation effects occur at ultrasonic powers lower and higher, respectively, than the cavitation threshold value.

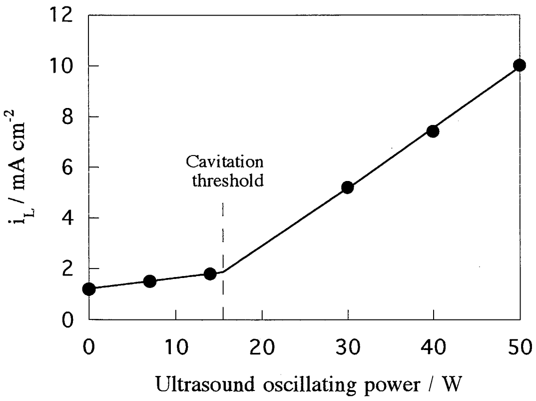


Figure 2. Relationship between limiting current density (i_L) and ultrasound oscillating power in the reduction of p-methylbenzaldehyde.

Coincidently with the cavitation intensity index, limiting current density (i_L) for the reduction of p-methylbenzaldehyde increases gradually with increase in the ultrasonic power (< 15 W) and steeply at > 15 W, as shown in Figure 2. A similar coincidence of the threshold value with a steep increase in i_L could be observed in the oxidation of hydroquinone. It is known that i_L is proportional to the mass transfer coefficient under diffusion control conditions. Therefore, it can be stated that mass transport in the electrode interface is promoted weakly and strongly by the acoustic field and cavitation effects, respectively.

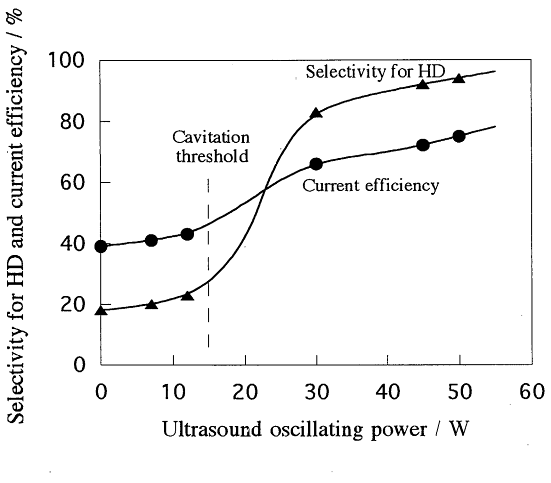


Figure 3. Dependence of ultrasound oscillating power on product selectivity for HD and current efficiency in the reduction of p-methylbenzaldehyde.

Furthermore, in our previous work,[14,18,20] it was also verified theoretically and experimentally that the current efficiency and product selectivity for the reduction of benzaldehydes arecontrolled by their mass transfer coefficients. As shown in Figure 3, both the current efficiency for HD + HM in the reduction of p-methylbenzaldehyde and the product selectivity for HD are also steeply increased at > 15 W conincident with the cavitation threshold value obtained in Figure 1. This fact indicates clearly that the efficiency and selectivity are affected more greatly by the cavitation effect than the acoustic effect.

In this study, it has been clarified that the significant effect of ultrasounds on the product selectivity and current efficiency occur at an ultrasound oscillating power lager than the cavitation thresfold value.

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