

# Electrochemical Hydrogenation of Alpha Methyl Styrene to Cumene

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A new hydrogenation process for atmospheric pressure conversion of alpha methyl styrene (AMS) to cumene is described. Formate ion is provided as a proton transfer agent in the reaction which involves AMS and water in the presence of a palladium catalyst. The bicarbonate ion, a product of the reaction is continuously reduced at the cathode of an electrochemical reactor to regenerate the formate. The influence of the emulsifying agent, formate concentration, applied potential and current density, the solution pH and temperature on the rate of AMS conversion is determined. Up to 96% AMS conversion was obtained at 60 °C.

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**Keywords:** mediated electrochemical reduction, alpha methylstyrene, cumene, bicarbonate-formate redox

## 1. INTRODUCTION

The primary method of production of phenol is the peroxidation of cumene. However, in this process, a significant proportion is lost as the byproduct  $\alpha$ -methylstyrene (AMS). While AMS by itself serves as a monomer for development of industrial polymers, in a phenol production plant, the primary aim is to maximize the yield of phenol. In addition, the separation and purification of AMS from the by-product stream is an added cost. Therefore, in order to increase the profitability of phenol plant, several manufacturers, such as Universal Oil Products, etc., have found it beneficial to hydrogenate AMS back to cumene and reintroduce it as the feed to the peroxidation process. The first industrial application for hydrogenation of AMS was commissioned in April 1979 at the Deer Park (Texas) plant of Shell Oil Co. In general, the hydrogenation of AMS is achieved via catalytic hydrogenation. However, this process requires the use of highly explosive hydrogen gas under high pressures (10-30 atm). In addition,

this reaction is limited by the diffusion of the gaseous hydrogen into the liquid phase and to the catalyst surface.

Hydrogenation of AMS is an irreversible reaction that produces cumene as the only product and is usually regarded first order in hydrogen and zero order in  $\alpha$ -methylstyrene when carried out in pure AMS at low pressures and temperatures [1-3]. However, due to operating problems of slurry type reactors and the difficulty of controlling aromatic losses, researchers had moved to fixed bed type reactors. The first of this kind to be commercialized was made by Engelhard Industries for Shell Oil Company. In the past, AMS hydrogenation has been conducted under various conditions of temperature and pressure using Pd/Al<sub>2</sub>O<sub>3</sub> or Raney nickel catalyst. Current commercial methods primarily employ a fixed bed [4] or a trickle bed reactor [5] to convert  $\alpha$ -methylstyrene to cumene. Whereas the slurry type reactor using a Raney nickel catalyst faces operating problems due to isopropylcyclohexane (IPCH) formation, fixed bed processes involving a three-phase system experience external mass transfer limitations [6-8]. In order to improve the AMS hydrogenation process by the use of supercritical CO<sub>2</sub>, a three phase catalytic system was employed with some success [9]. Even with 11 atm of H<sub>2</sub>, a maximum of 80 % conversion was possible without the use of supercritical CO<sub>2</sub> after 120 minutes of reaction. It is reported in one study [10] that the conversion of AMS to cumene could be increased by 60 % in a trickle bed reactor by operating in a high interaction regime rather than in a trickling regime, primarily due to the increase in the mass transfer rates. Recent studies on the hydrogenation of  $\alpha$ -methylstyrene to cumene using a monolithic reactor have predicted a range of reaction rates [11, 12] under similar operating conditions which points to the fact that non-uniform or incomplete catalyst wetting might be a possible parameter for partially controlling the conversion. Also, a possible influence of inhibitors like water seems to affect the rate of the reaction which accounts for the discrepancies in the reported hydrogenation rate. In addition, the use of high pressure H<sub>2</sub> present operational hazards such as explosion. More importantly, the production of hydrogen is realized through the steam methane reforming. The process results in significant release of CO<sub>2</sub>, a greenhouse gas (GHG) that has been identified as the cause of climate change. This factor alone may suffice for the search of an efficient zero-carbon process such as that driven by electrochemical reactions power by solar energy. Electrochemical hydrogenation of 4-methyl styrene [13] to 4-ethyltoluene was studied in a two-compartment electrochemical cell, which involved reduction using hydrogen produced by water electrolysis.

As mentioned earlier, the use of an electrochemical pathway may provide a near-zero GHG emission solution if comparable conversions are achieved to conventional methods at similar or more benign conditions. Electrolytically produced hydrogen may result in low carbon H<sub>2</sub> production method, but the issue of low diffusion of hydrogen may result in lower conversion. An alternative to the use of molecular H<sub>2</sub> as the source for hydrogen is to use chemicals that can readily donate hydrogen to the catalyst at ambient pressures and low temperatures. This method of hydrogenation is commonly known as catalytic transfer hydrogenation (CTH). Some of these chemicals include primary and secondary alcohols, formic acid, formate, etc. A study documenting the hydrogenation of AMS using isopropyl alcohol as the donor and IrCl<sub>3</sub> (Me<sub>2</sub>SO)<sub>3</sub> as the catalyst was carried out [14]. However, the yield of cumene was only 12 %. A subsequent study [15] employed the same approach as described in [14] where indoline was used as the donor and Pd/charcoal as the catalyst. These were the only two reported

attempts of using chemical transfer methods for hydrogenating AMS. Relatively more recently, Rh-amine complex on SiO<sub>2</sub> was imprinted to carry out shape-selective catalysis of AMS [16].

Even though the limited studies did not show comparable hydrogenation rates using CTH, the process can be exploited to regenerate the hydrogen donor *in situ*. In such a process, the donor (DH<sub>2</sub>) essentially acts as a shuttle for the hydrogen from the electrode surface where its oxidized form picks up the hydrogen ( $D + 2H^+ + 2e^- \rightarrow DH_2$ ) and then diffuses to the catalyst surface to react with substrate (A) and get oxidized ( $A + DH_2 \rightarrow AH_2 + D$ ) and thus may be viewed as a mediator for hydrogen or an electrocatalyst in the electrochemical process. In this paper, we present the kinetics of CTH of AMS using a simple hydrogen donor – formate- which can be regenerated from its oxidized form – bicarbonate – at the cathode. We further present the use of the donor as a mediator. A mediator assisted electrochemical hydrogenation process that uses such a donor for hydrogenating unsaturated fatty acids in vegetable oils and regenerating the oxidized form of the donor at the cathode has been reported [17 - 20]. Microemulsion of oil in water containing formic acid and nickel hydrogenation catalyst placed in the cathode compartment subjected to an electrical current undergoes hydrogenation at temperatures as low as 45°C. Formate ion was used as a shuttle for transferring hydrogen to the surface of a hydrogenation catalyst (7 % Ni/ SiO<sub>2</sub>) where the oil (soybean, canola) was reduced with significantly low levels of isomerization (the production of deleterious *trans* fatty acid was greatly reduced). The formate ion was regenerated at the cathode and thus acted as a mediator for the hydrogenation process. The application of a current density of 10 mA/cm<sup>2</sup> resulted in hydrogenated product with desired fatty acid composition. In this paper, we also present the results of mediator assisted electrochemical hydrogenation of AMS under ambient pressures and relatively low temperatures in a divided electrochemical cell with unequal compartments.

## 2. EXPERIMENTAL

The AMS and cyclohexane were obtained from Fisher Scientific (Chicago, IL). Didoceyl dimethyl ammonium bromide (DDAB), a surfactant and emulsifier was obtained from Fluka (St. Louis, MO) and sodium formate (99.8 %), formic acids (97%) and 1 % Pd/γ-Al<sub>2</sub>O<sub>3</sub> were obtained from Alfa Aesar (Ward Hill, MA). All chemicals were of reagent grade and used as received.

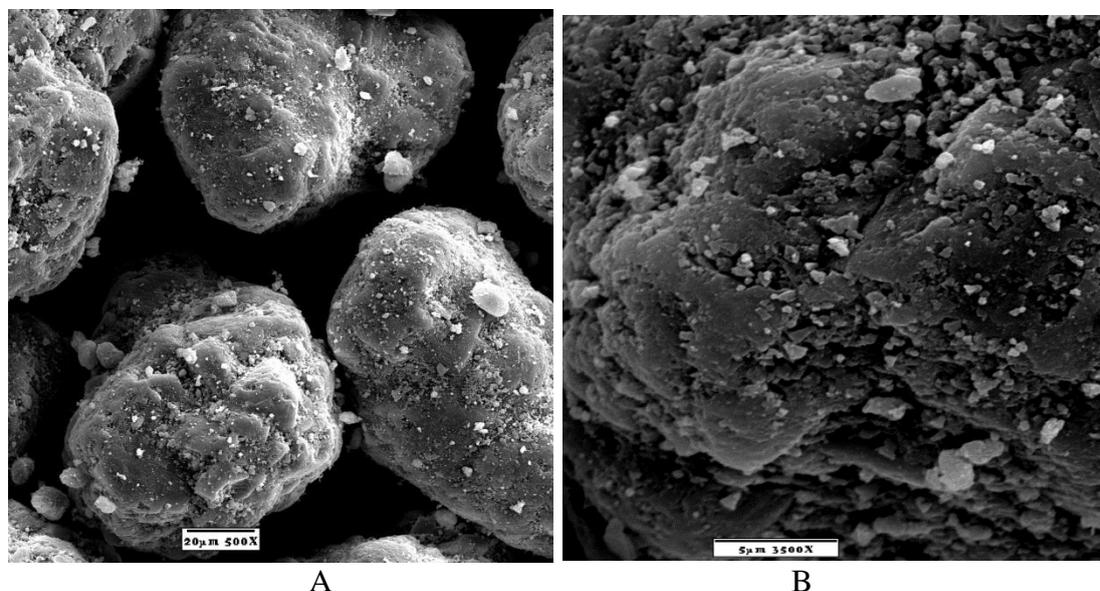
Catalytic transfer hydrogenation experiments were carried out in batches of 50 mL using conical Erlenmeyer flasks. In a typical experiment, a predetermined amount of emulsifier, DDAB was added to a mixture of AMS in cyclohexane and water. The mixture was then stirred to form a microemulsion. Once the microemulsion was observed, a predetermined amount of the hydrogen donor (formate) was added followed by the addition of the hydrogenation catalyst (1 % Pd/ α-Al<sub>2</sub>O<sub>3</sub>). The experiments were typically conducted for 180 minutes (except for the kinetic studies). At the conclusion of the experiment, the three-phase mixture was decanted (through a filter paper of pore size 2.5 μm) to remove most of the aqueous phase as the filtrate. The organic phase-catalyst mixture was then collected and centrifuged at 3200 rpm in a Marathon 8K Centrifuge (Fisher Scientific) for 5 min to separate the catalyst and any remaining water from the organic phase. The AMS/cyclohexane/cumene mixture was analyzed for its composition using a gas chromatograph (Buck Scientific, St Louis, MO). Laboratory standards of α-

methylstyrene, cumene and were used to determine their retention time and calibration. Helium was used as the carrier gas, at a pressure of 30 psig. The injector and the detector temperatures were kept at 200°C and 170°C respectively. The peaks obtained from an analysis of a sample of the product mixture were checked for their areas and the relative concentration of the  $\alpha$ -methylstyrene and cumene calculated from it as a percent sum of all the peak areas.

The electrochemical experiments were carried out in a batch electrochemical reactor described in previous studies [17-20]. A 150 ml reactor with a length to diameter ratio of 2.95 was used. The anode chamber occupied 10 ml of anolyte in a tube with 0.5 in diameter and was separated from the cathode chamber by a fine glass frit that prevented any organic material from entering the cathode chamber. The resistance to the diffusion of ions across the membrane was negligible. Both, the anode and the cathode comprised of platinum mesh or graphite felt. The cathode was 1 inch square while the anode was 0.5 in x 2 in rectangle. A standard calomel electrode was used as the reference electrode. A magnetic stirrer provided agitation to disperse the oil in the electrolyte solution and create a microemulsion.

In a typical experiment, the required amount of the electrocatalyst (mediator or hydrogen donor) was added to the beaker containing a mixture of AMS in cyclohexane and water. A solution of 5 g/L of NaCl was added to decrease the electrical resistivity of the mixture. This was followed by the addition of the emulsifier, DDAB. The mixture was then stirred and heated to the specified temperature in a water bath. The hydrogenation catalyst, 1 % Pd/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, was then added. A Gamry Instrument 750 PC3 potentiostat/galvanostat was used to carry out the experiments. For the preliminary studies, experiments were carried out for 45 minutes. All other experiments were conducted under constant potential or constant current condition for 3 hrs. The organic component extraction and quantification of the composition of the product mixture was achieved similar to the post CTH procedures.

### 3. RESULTS AND DISCUSSION



**Figure 1.** SEM image of (a) Pd/Al<sub>2</sub>O<sub>3</sub>, 500X and (b) coated Pd/Al<sub>2</sub>O<sub>3</sub>, 3500X

Figure 1 contains the SEM photomicrographs of the Pd/ $\gamma$ -alumina catalysts at a magnification of 500 and 3500 using the backscatter mode to observe the Pd deposits on the alumina samples. The photomicrographs show the presence of nanometer deposits. The data show the presence of about 80  $\mu\text{m}$  sized particles. Also, the Pd deposits generally cover a fairly large surface area of the alumina substrate

### 3.1. Hydrogenation Studies

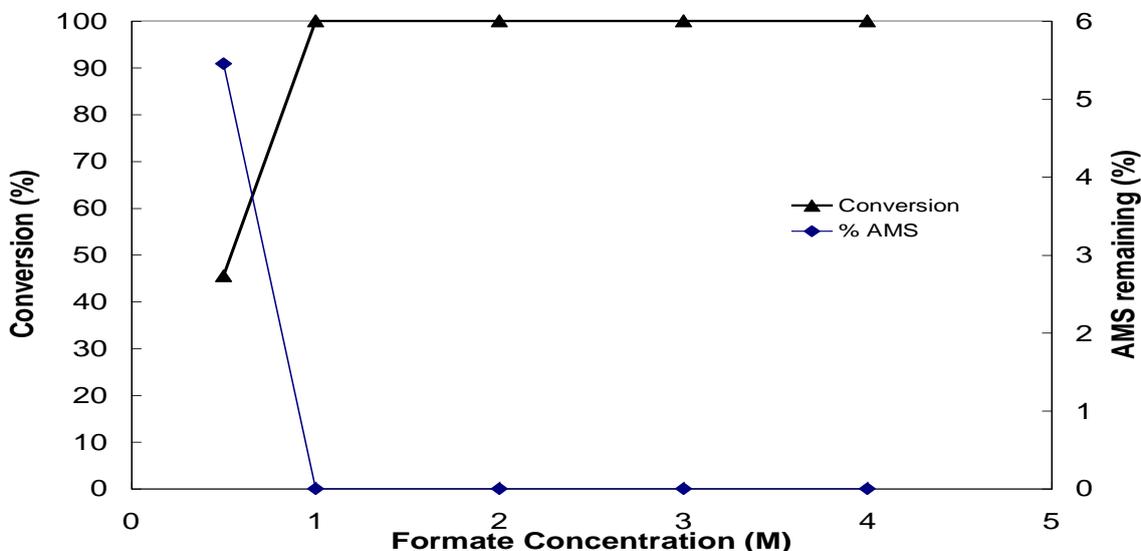
Since the reaction mixture is heterogeneous consisting of three phases (aqueous, organic liquid and solid catalyst), the rate of agitation is expected to have significant influence on the overall rate of CTH reaction. No electric field was applied in these studies. As anticipated, no reaction was observed under quiescent conditions. The rate was observed to increase with the extent of agitation until a stirring rate of 521 rpm was maintained, however, at higher stirring speeds AMS conversion was found to be independent of the extent of agitation. Thus, it is assumed that at speeds lower than 521 rpm the reaction rate is limited by the mass transfer effects. Subsequently, all experiments were carried out at a constant stirring rate of 600 rpm.

### 3.2. Chemical Hydrogenation: Effect of Donor concentration

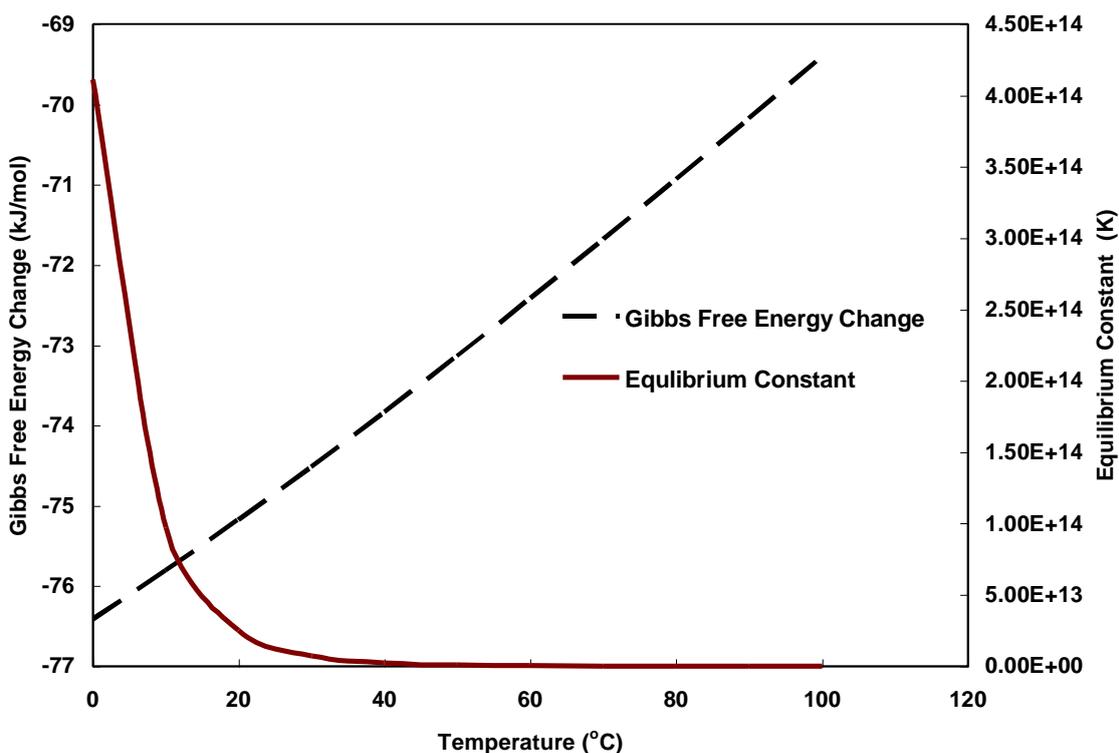
Experiments were conducted to study the influence of the hydrogen donor (i.e. formate) on AMS hydrogenation which involved the use of 50 ml of a three-phase mixture (30% organic fraction) containing 10 % AMS in cyclohexane with 0.04 g/L of emulsifier of DDAB at 25°C and ambient pressure. A catalyst loading of 25 g/L Pd/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was employed. It must be noted that in the absence of cyclohexane (i.e. organic phase), no AMS conversion was observed, a result which is consistent with findings from reports related to molecular hydrogenation [2-3] of AMS. The explanation offered for the use of cyclohexane is that its use helps dissipates the heat of reaction. In the formate-water reaction system, dispersion of heat is not an issue due to the presence of excess amount of water leading to conclusion that the non-polar solvent of cyclohexane of low dielectric constant plays an important part in dissolving the reactant (i.e. AMS) so as to enable its hydrogenation either by molecular hydrogen or formate. Hydrogenation of nitroarenes to aminoarenes using formate salts as hydrogen donors and Pd/C as catalyst in liquid/liquid/solid system using isotopes of various reactants (formate, water) has been reported in the literature [21]. It was clearly demonstrated that the hydrogen molecule is formed by combination of a hydride originated from the formate and proton supplied by the water. Thus, the system actually incorporates two donors (water and formate). In our experiments, the absence of water in the reaction mixture led to no AMS conversion. Thus, we believe water is also essential for hydrogenation.

Figure 2 is a plot of the extent of AMS conversion vs. the formate concentration in the reaction mixture under the open circuit conditions, i.e. CTH. The data show that a minimum of 1 M donor concentration is required for complete conversion within 180 minutes. Excess amount of formate is required since some formate decomposes on the catalyst surface yielding molecular H<sub>2</sub>, which is lost. In addition, since AMS hydrogenation occurs on the surface of the catalyst, the competitive adsorption of the formate and AMS could determine the rate of reaction. In addition to the concentrations of AMS and

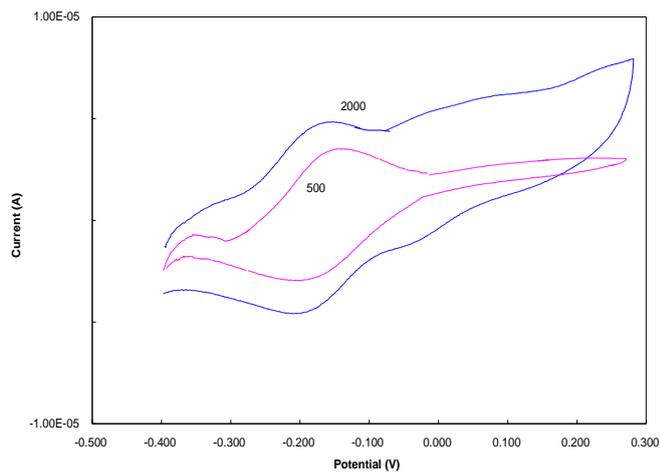
water, the rate of reaction is also proportional to the formate concentration which decreases over the course of time thus necessitating excess donor content to ensure a rapid reaction rate. Nonetheless, the results clearly show that CTH is a potentially feasible route for AMS hydrogenation using formate as a donor.



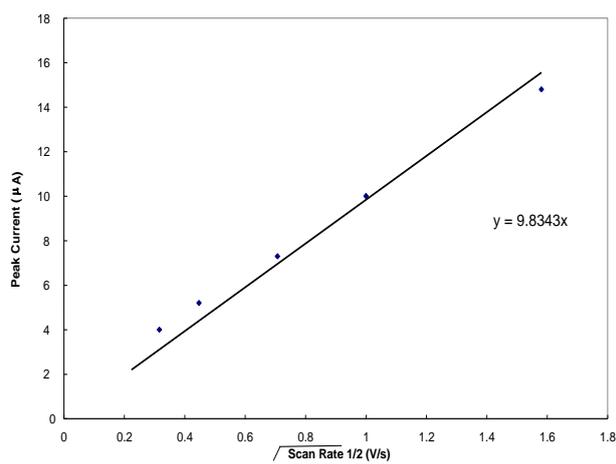
**Figure 2.** Effect of donor (HCOONa) on the extent of AMS hydrogenation (10 % AMS in cyclohexane, organic fraction 0.3, 0.04 g/L DDAB, 25 g/L Pd/□ Al<sub>2</sub>O<sub>3</sub>, pH =7, reaction time =180 min).



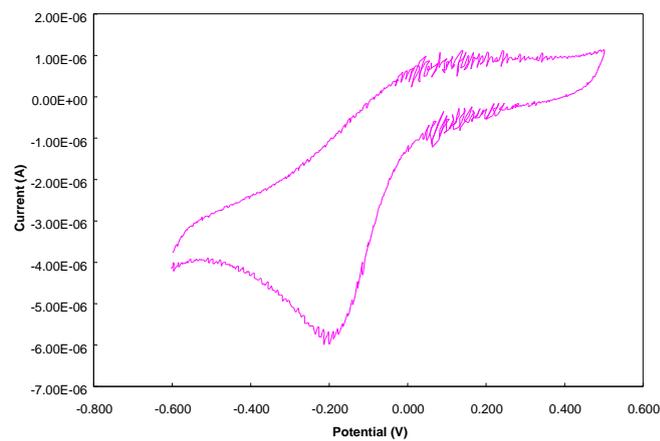
**Figure 3.** Temperature vs. Gibb’s Free Energy and Equilibrium Constant.



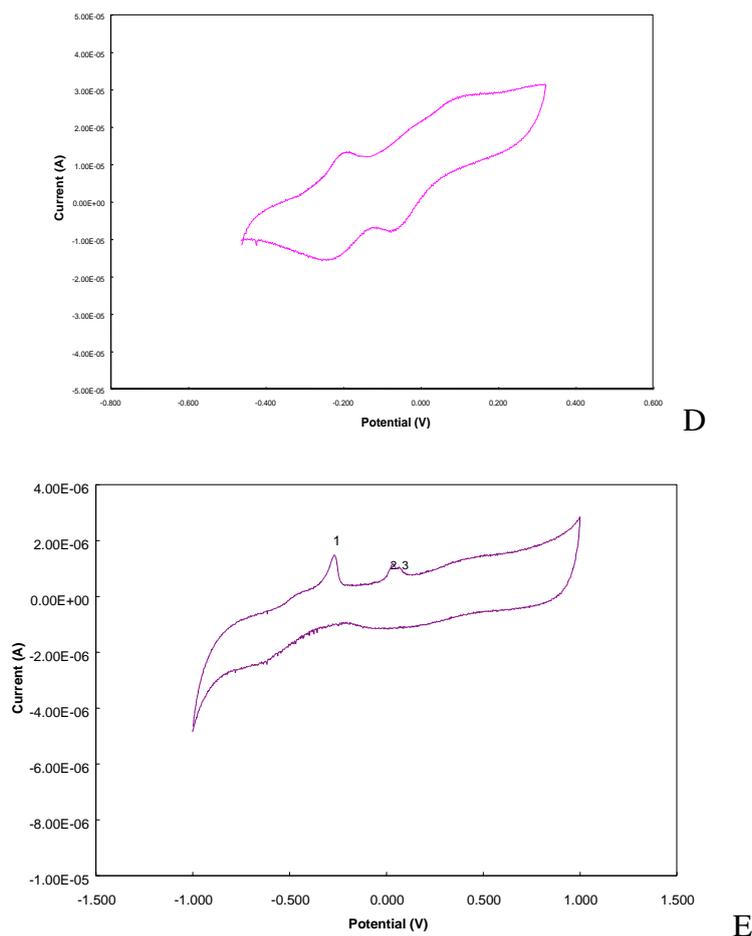
A



B



C



**Figure 4.** Effect of scan rates on CVs of formate/bicarbonate redox couple conducted at 45 °C (a) scan rates of 200 and 500 mV/s; b) effect of peak current; (c) scan rate of 5 mV/s; (d) 2000 mV/s and (e) scan rate of 500 mV/s on glassy carbon.

This process is competitive with conventional hydrogenation methods of AMS at ambient temperature and pressures as opposed to the results on other CTH studies reported earlier [14, 15].



Figure 3 is a plot of temperature of the reaction vs. the Gibb's free energy change for the reaction shown above. We used HSC Chemistry5.1 software to calculate the values. At ambient temperature, the Gibb's free energy change of the reaction is negative indicating that the reaction is spontaneous. Thus, almost no energy expenditure is needed to produce AMS from cumene as long as formate ion is available to drive the reaction to the right-hand side. The equilibrium constant is found to increase with a decrease in temperature indicating higher degree of conversion to cumene at lower temperatures, if the reaction is equilibrium limited.

The experiments described below list an electrochemical approach to concomitantly regenerate formate anion from the bicarbonate at the cathode of a reactor. Formic acid (formate anion) has been

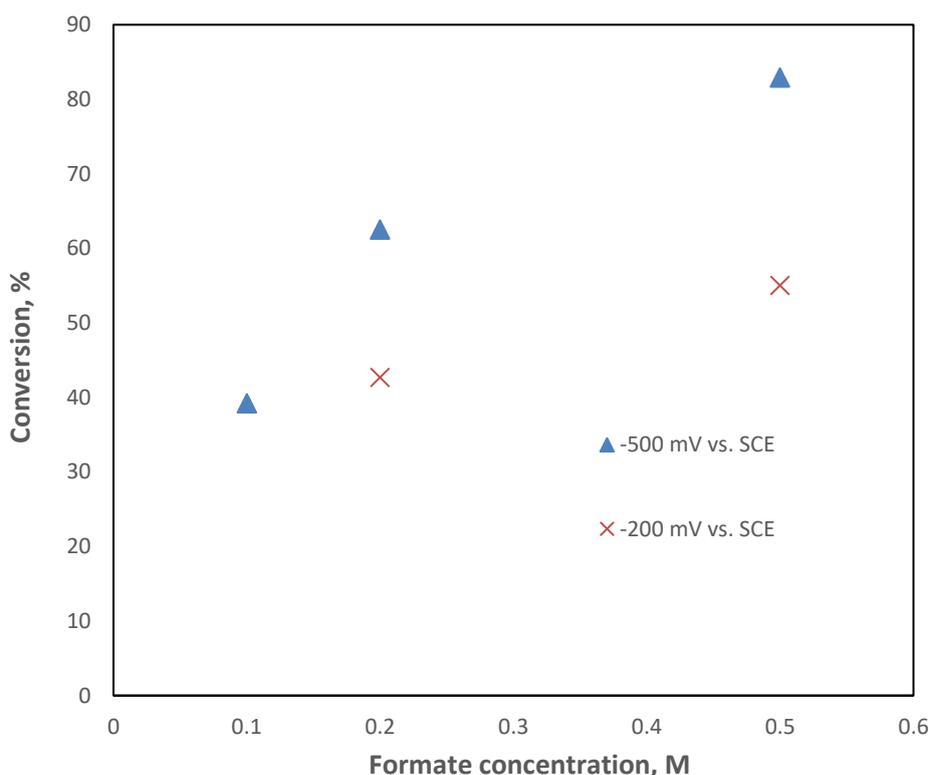
shown to be an excellent mediator for hydrogenation of vegetable oils [18]. Catalytic reduction of  $\text{HCO}_3^-$  to  $\text{HCO}_2^-$  has been demonstrated [24 - 26]. Electrochemical studies [19, 24, 27-29] have documented the oxidation and reduction behavior of the formate/bicarbonate couple at the electrodes. It was shown that chemically derivatized electrodes could reduce bicarbonate ions to formate at the thermodynamic potential [30]. More recently, a study [31] on the electrochemical reduction of  $\text{CO}_2$  and  $\text{HCO}_3^-$  ion on copper showed that the bicarbonate ion essentially reduces to formate ion if the hydrogen evolution reaction could be minimized. The importance of bicarbonate ion in electrochemical reduction of aqueous solution of  $\text{CO}_2$  to formate was also reported [32]. Cyclic voltammetry studies on bicarbonate/formate couple further elucidate the mechanism of the oxidation and reduction reactions [33]. It has also been shown that the formate/bicarbonate,  $\text{HCOO}^-/\text{HCO}_3^-$  form a redox couple [20]. Therefore, it will be able to behave as a mediator in the electrochemical reduction of the  $\alpha$ -methylstyrene.

Cyclic voltammetry studies were conducted on formate-bicarbonate mixtures. Cyclic voltammograms obtained for scan rates of 500 and 1000 mV/s are presented in Figure 4a. It is observed in the figure that the  $E_{pa}$  and  $E_{pc}$  are  $-0.173$  V vs SCE and  $-0.231$  V vs. SCE, respectively. The formal reduction potential of the bicarbonate ion at  $25^\circ\text{C}$  is  $-0.239$  V vs SCE while that of the oxidation of the formate ion to the carbonate ion and carbon dioxide are  $-0.140$  and  $-0.017$  V vs. SCE, respectively. The reduction potential value is very close to the hydrogen/water couple. The peak currents obtained from the studies at different scan rates were plotted against the square root of the scan rate and presented in Figure 4B. A straight line was fitted to the points via linear regression. The fitted line passed through the origin and had a slope of 9.83. The diffusivity coefficient of the formate anion was estimated to be approximately equal to  $0.9 \times 10^{-5}$   $\text{cm}^2/\text{s}$ . While the voltammograms presented in Figure 4A show one oxidation and one reduction peak each, additional studies conducted revealed some interesting facets of this couple. Figure 4C is a cyclic voltammogram conducted at a scan rate of 5 mV/s. As seen in Figure 4C, no oxidation peak was observed for very low scan rates. The reason for this observation is the decomposition of formic acid at the surface of metals such as platinum. As a result, the newly formed formic acid is converted chemically to bicarbonate at the surface before the scan is reversed and the oxidation potential is reached. At very high scan rates, an additional reduction peak at a potential of  $-0.058$  V vs. SCE was observed in the voltammograms (Figure 4D). This peak is probably due to the direct reduction of carbonate. Figure 4E is a voltammogram obtained using glassy carbon electrodes. No reduction peaks are observed. However, two clear oxidation peaks, 1 and 2 are observed. Two observations are made by examining Figure 4E. The first is that for the reduction of bicarbonate, it is necessary to use an electrode capable of adsorbing hydrogen which is consistent with results shown in literature [30]. The second is that in addition to the bicarbonate formation, the subsequent carbonate or carbon dioxide formation occurs when the electrode potential is made more anodic. Thus, platinum electrode and a porous carbon electrode (graphite felt) was used in electrochemical hydrogenation studies.

### 3.3. Mediator Assisted Electrochemical Hydrogenation Process: Preliminary Results

Experiments were conducted by varying the formate concentration and the applied electrode potential. A typical experiment constituted an organic fraction which contained 10% AMS by volume

to which an aqueous phase containing 0.04 g/l of emulsifier (DDAB) was added so that the resultant organic fraction in the total mixture was 0.3. The initial solution pH was 7. A Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst of 25 g/l loading was added to the reaction mixture which was thoroughly stirred over the course of experiments (3 hours). Under the open circuit potential conditions, 42.7% conversion of  $\alpha$ -methylstyrene was obtained when the initial formate concentration employed was 0.5 M. Figure 5 shows the influence of formate addition on conversion at two different potentials. The preliminary data show that conversion of  $\alpha$ -methylstyrene increases with the addition of formate ion and application of more negative potential (i.e. reducing conditions). As compared to the conversion (42.7%) obtained under the open-circuit conditions, higher conversion (82.9%) representing an increase of 94% increase in conversion, is obtained for an experiment conducted at -500 mV vs. SCE.



**Figure 5.** Conversion as a function of formate concentration and applied potential (10 % AMS in cyclohexane, organic fraction = 0.3, pH =7, 0.04 g/L DDAB, 25 g/L Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Pt electrodes).

It must be added that less than 1 % conversion was observed when the experiment was conducted at an applied potential of -500 mV in the absence of the formate ion. Thus, it is unlikely that molecular hydrogen generated electrolytically resulted in significant hydrogenation. Since the residence time of molecular hydrogen in the reactor system is expected to be negligible as compared to the reaction time needed for the AMS hydrogenation, the lack of conversion in the absence of formate ion is not surprising. In addition, the low pressure of hydrogen will reduce its solubility in the reaction mixture as well as its diffusivity. The above findings suggest that the presence of hydrogen donor is essential for AMS conversion. Since,  $\alpha$ -methylstyrene can be hydrogenated under open-circuit conditions, it can be

concluded that the reaction pathway is chemical in nature. In the presence of an applied potential (current), formate is regenerated at the cathode thus fostering enhanced rates of reaction.

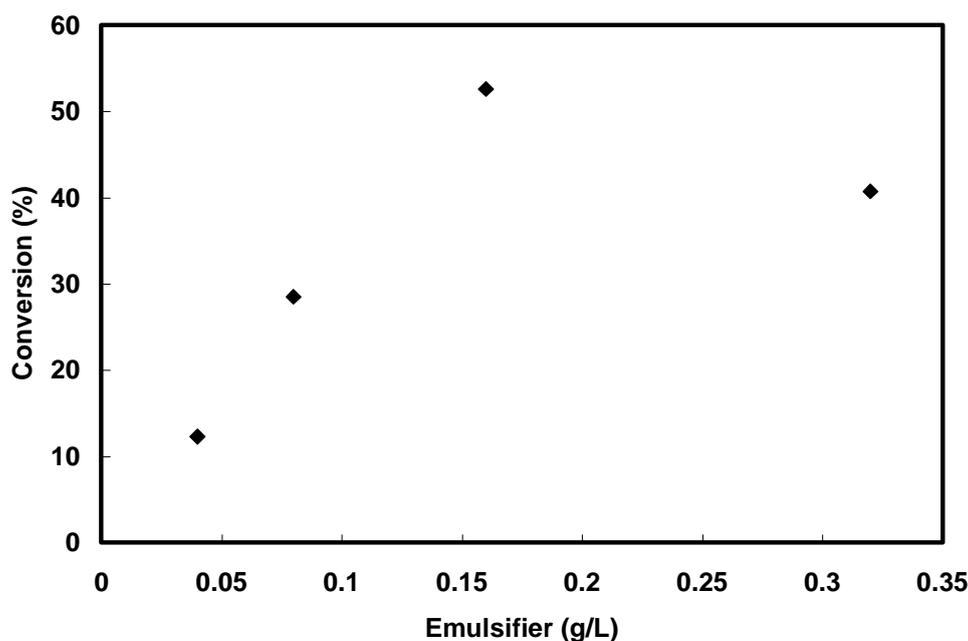


The above cathodic reaction must have its counterpart anodic reaction. The most plausible reaction at the potentials employed in this study involves oxygen evolution and proton formation from the water molecule according to the following reaction



### 3.4. Emulsifier

Didodecyl dimethyl ammonium bromide (DDAB), a non-micellar forming surfactant was utilized for creating the microemulsions [19]. Past studies have clearly demonstrated the improvement in selectivity via the use of microemulsions. However, very little research has been conducted with microemulsions despite their higher solute capacity, lower toxicity and often low cost (when compared against the overall benefits). Quaternary ammonium salts, such as DDAB and cetyl trimethyl ammonium bromide (CTAB), as phase transfer catalysts in microemulsions for electrosynthesis have been reported in the literature [22, 23]. The following narrative relates to the effect of emulsifier concentration on the process performance

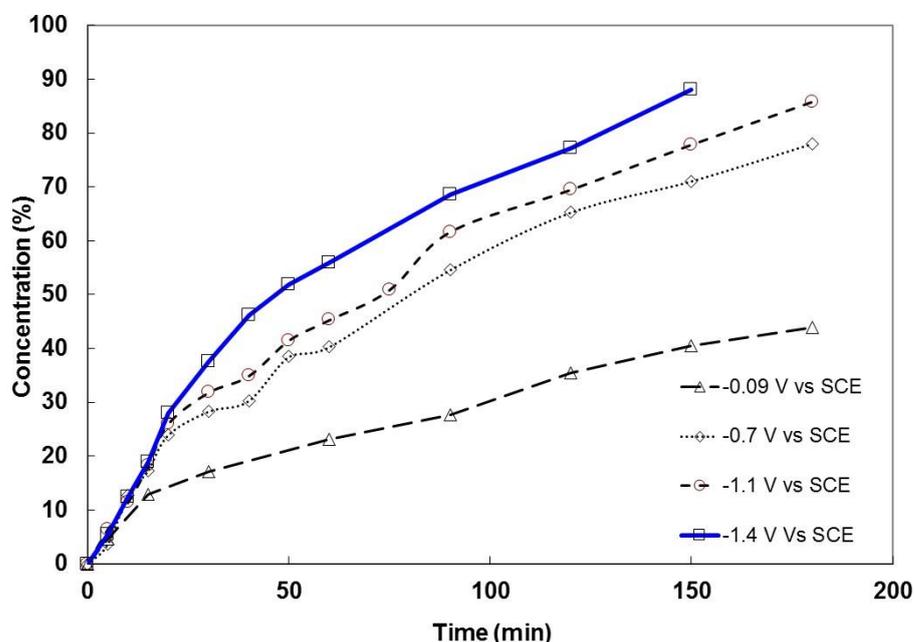


**Figure 6.** Influence of emulsifier concentration on the extent of hydrogenation of AMS using the MEH process (10 % AMS in cyclohexane, organic fraction = 0.3, pH =7, 0.5 M HCOONa, 25 g/L Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Pt electrodes)

Experiments were conducted for a period of 45 minutes at a constant potential of -500 mV vs. SCE by employing a reaction mixture to which 0.5M formate was added. Data in Figure 6 shows that  $\alpha$ -methylstyrene conversion increased from 12.3 to 52.6% when the emulsifier (i.e. DDAB) concentration was increased from 0.04 to 0.16 g/l. A further increase in the emulsifier concentration to 0.32 g/l resulted in a slight decrease in AMS conversion. The extent of emulsification is directly related to the DDAB content, and thus, it corresponded to the rate of AMS hydrogenation. However, DDAB also participates in competitive adsorption with AMS, formate and other species present in the reaction mixture for the active sites available on the catalyst surface. As the concentration of DDAB is increased in the solution, the number of sites available for other reactants, namely AMS is lowered and as a result corresponding decrease in the reaction rate is observed.

### 3.5. Potentiostatic Experiments

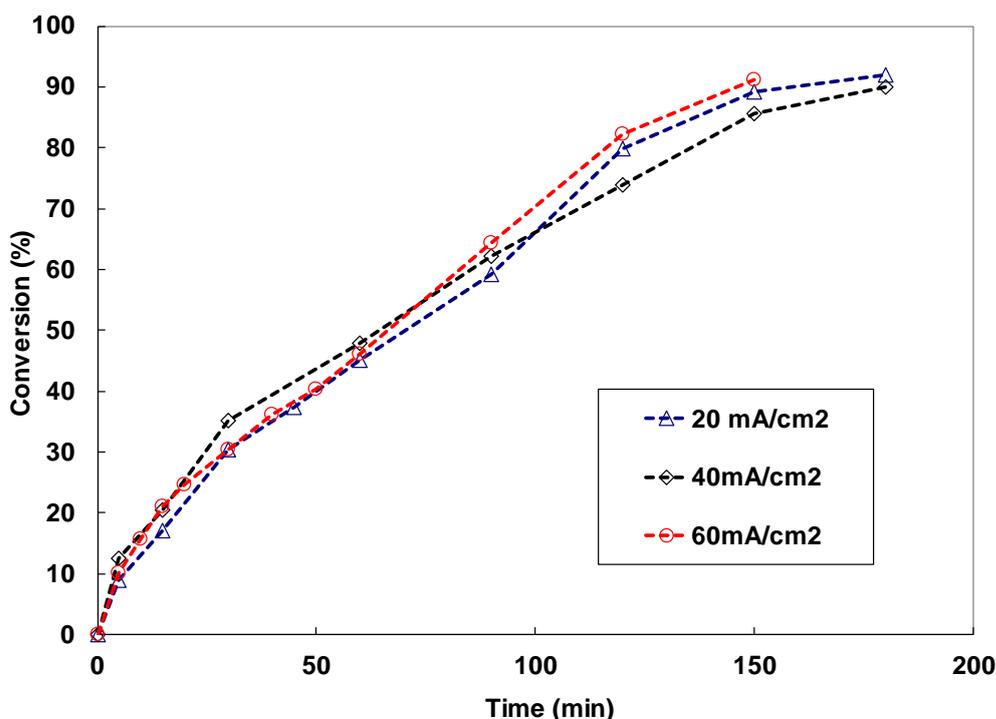
Experiments described in this section were conducted at constant potentials ranging from -0.09 to -1.4 V vs. SCE (Figure 7).



**Figure 7.** Influence of potential on the extent of hydrogenation of AMS using Pt cathode (0.5 M formate, 10 % AMS in cyclohexane, 0.16 g/L of DDAB and 20 g/L Pd/g- $\text{Al}_2\text{O}_3$ , pH =7).

A decrease in the applied potential (under more reducing conditions) led to a corresponding enhancement in AMS conversion. For example, greater than 80% increase in conversion was observed when the potential maintained at a platinum electrode was lowered from -0.09 to -1.4 V vs. SCE. It must also be noted that when no formate was employed, negligible AMS conversion was observed leading to the conclusion that direct electroreduction of AMS at the cathode is not a viable reaction under the experimental conditions employed in this study (not shown in the figure). The use of graphite felt cathode also resulted in AMS conversion which increased with lowering of the cathodic potential.

Although electrochemical hydrogenation of 4-methyl styrene [13] to 4-ethyltoluene is reported in the literature, it must be noted that the mediator-assisted electrochemical hydrogenation process discussed here is different. According to the reaction scheme described by Iwakura and his coauthors [13], water electrolysis led to the production of protons at the palladium cathode which diffused to the outside of the reactor (i.e. the back of the cathode which was palladinized by a chemical treatment) to the outer chamber that contained the reactant. Reduction of styrene by the protons led to ethyltoluene formation. We have hypothesized a mediator-assisted mechanism for hydrogenation as discussed above, which is in line with the reaction pathways reported previously that employ formate ion as an electron shuttling agent [17-20].



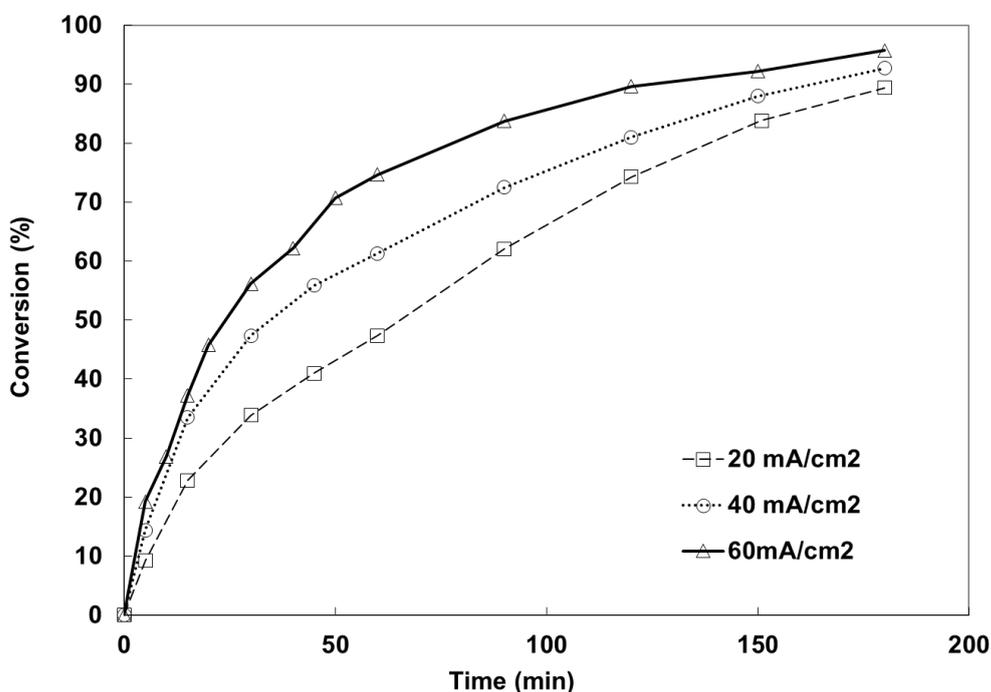
**Figure 8.** Influence of current density on the extent of hydrogenation of AMS using Pt cathode (0.5 M formate, 10 % AMS in cyclohexane, 0.16 g/L of DDAB and 20 g/L Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, pH =7).

The data presented in Figure 4 along with the negligible hydrogenation in the absence of formate ions justify the hypothesized mechanism.

### 3.6. Galvanostatic Experiments

The influence of the applied constant current density on AMS hydrogenation was also studied in experiments involving platinum as well as graphite felt cathodes. Current densities of 20, 40 and 60 mA/cm<sup>2</sup> were impressed for a period of 3 hours. In general, it is observed (Figures 8 and 9) that the AMS conversion increased with the magnitude of the applied current. An increase in the cathodic current (i.e. more reducing conditions) led to a corresponding advancement in formate regeneration. As a result, the hydrogenation rate at the catalyst surface, which is a function of the formate concentration, was

maintained at a high level. Thus, at higher current densities, the rate of hydrogenation is observed to be greater. For example, in the case of platinum cathode when the current density was increased three-fold, from 20 to 60 mA/cm<sup>2</sup>, a corresponding increase in 2 % conversion was observed over the course of 50 minutes. Similarly, for the experiments employing graphite felt cathode, a 75% enhancement in the AMS conversion was obtained upon a three-fold increase in the current density from 20 to 60 mA/cm<sup>2</sup> in 50 minutes.



**Figure 9.** Influence of current density on the extent of hydrogenation of AMS using graphite felt cathode (0.5 M formate, 10 % AMS in cyclohexane, 0.16 g/L of DDAB and 20 g/L Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, pH =7).

The data also show that as compared to platinum, the use of graphite felt cathode resulted in greater rate and extent of AMS conversion. The above observations can be explained by considering the following parasitic reaction involving hydrogen evolution, in addition to the electrochemical reaction necessary for the formate regeneration:

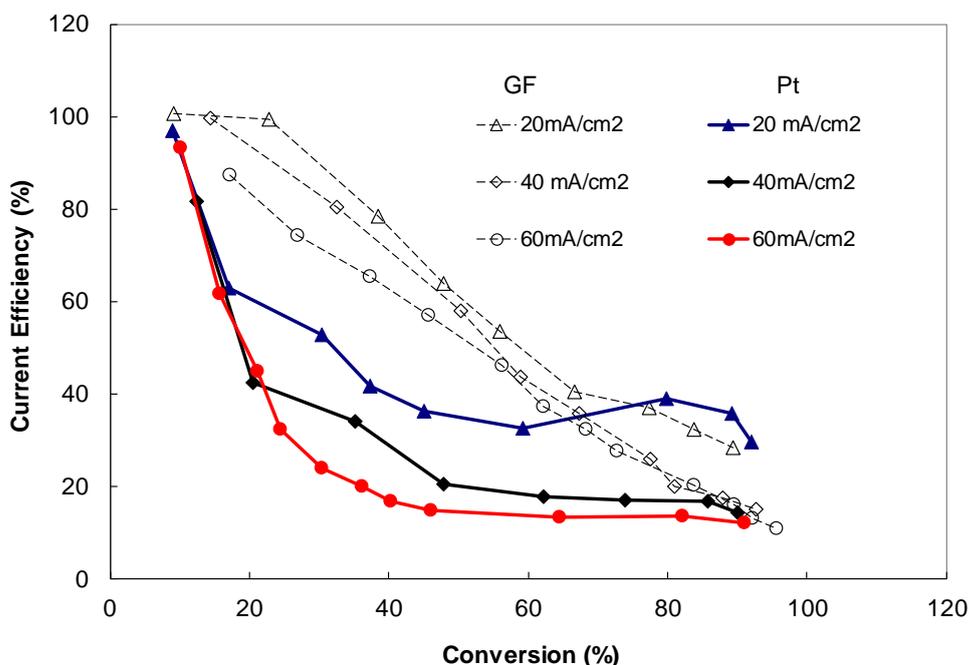


An increase in the current (potential) leads to higher rates of hydrogen evolution which competes with the formate regeneration reaction [27, 30]. In addition, the presence of hydrogen gas bubbles near the cathode surface could pose mass transfer limitations to movement of bicarbonate and formate between the bulk and electrode, thus, resulting in lower overall rates of AMS hydrogenation. Since, hydrogen evolution is kinetically favored at the platinum electrode, the corresponding increase in AMS conversion is lower as compared to the one observed for experiments involving the use of graphite felt electrodes.

Further confirmation of the above explanation is obtained by examining the Faradaic efficiency vs. time data (Figure 10). Faradaic efficiency is defined as the ratio of electric charge corresponding to the amount of a product obtained to the actual total charge passed through the electrochemical reactor:

$$\eta = (nFN_0)/Q \quad (5)$$

where,  $n$  is the number of electrons transferred during an electrochemical reaction,  $F$  = Faraday's constant,  $N_0$  is the number of moles of product, and  $Q$  is the electric charge obtained by integrating current over time.



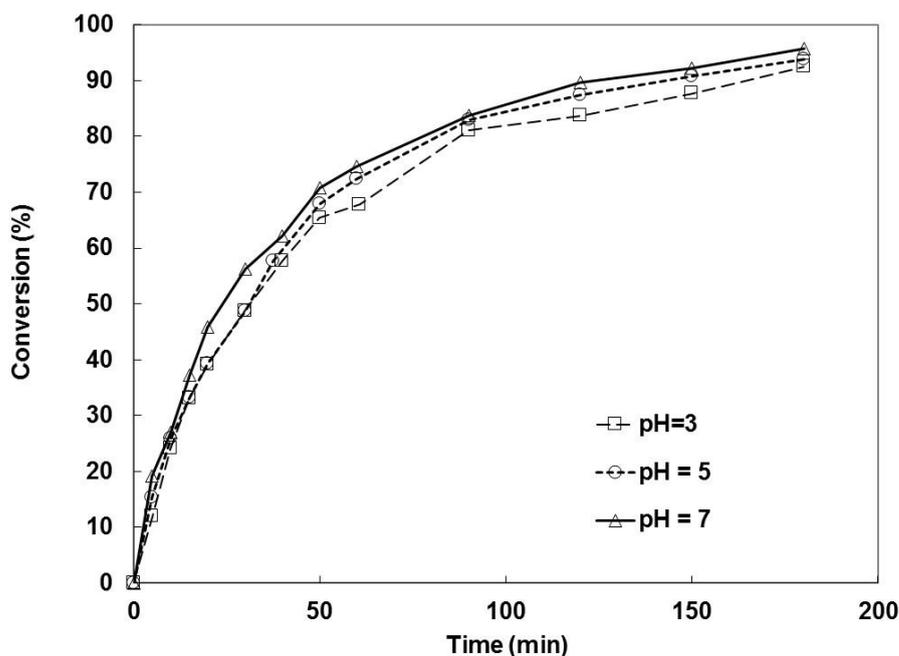
**Figure 10.** Current efficiency as a function of time for 3 applied current densities (0.5 M formate, 10 % AMS in cyclohexane, 0.16 g/L of DDAB and 20 g/L Pd/g-Al<sub>2</sub>O<sub>3</sub>, pH =7).

The data show that, for both, platinum as well as graphite felt cathodes, initial faradaic efficiency is relatively high for AMS conversion, and it is even more so when a graphite felt is employed as a cathode. However, the efficiency is observed to decrease sharply with time. At relatively high extents of conversion (above 80%), the Faradic efficiency for both, the platinum as well as the graphite electrode, is just about the same. This has to do with the fact that when the reactant is nearly exhausted, hydrogen evolution reaction is predominant, since the bicarbonate ion is no longer available for reduction at the cathode.

In general, the following observations can be attributed to the evolution of hydrogen gas: (i) lower efficiency at high current densities, and (ii) lower efficiency for AMS conversion on platinum as opposed to graphite cathode.

### 3.7. pH Effect

The AMS conversion as a function of time was studied in three experiments conducted at pH values of 3, 5 and 7 (Figure 11). An applied current density of  $60 \text{ mA/cm}^2$  was impressed upon the electrochemical reactor. The data show that although nearly 100% conversion is observed for all experiments conducted for 180 minutes, however, the reaction rate is marginally greater for those experiments which had the low initial solution pH. The high proton concentration at low pH is expected to facilitate formate regeneration via equation (2). In order for the hydrogenation reaction to occur, adsorption for formate and AMS on the catalyst is essential.



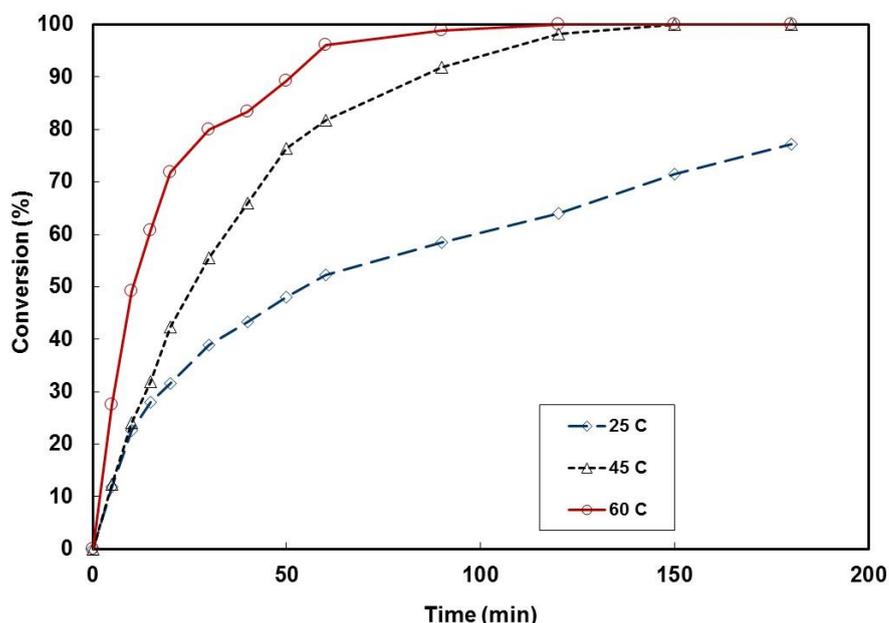
**Figure 11.** Influence of pH on the extent of hydrogenation of AMS using Pt cathode (0.5 M formate, 10 % AMS in cyclohexane, 0.16 g/L of DDAB and 20 g/L Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 60 mA/cm<sup>2</sup>).

At high pH (i.e. 7), the relative low concentration of H<sup>+</sup> results in less competitive adsorption of protons thus resulting in higher formate and AMS adsorption as compared to the case when the solution pH is low (e.g. 3). This, may, in part explain as to why at even relatively high pH (5 and 7), the rates of reaction are significant although the rate of formate regeneration can be expected to be low.

### 3.8. Temperature

Experiments were conducted at 35, 45 and 60°C at a potential of -1.4 V vs. SCE using both, platinum as well as graphite felt cathodes. The data (Figure 12) shows that conversion increased with temperature. For example, only 52.4% AMS conversion was observed in 60 minutes at 25°C, however, when the temperature was raised to 60°C over 96% conversion was achieved. The increase in the overall reaction rate with temperature can be attributed to enhancements in reaction rates of the following

individual rates: (i) electrochemical regeneration of formate, (ii) catalyst surface reaction, and (iii) overall mass transfer rate. Similar, albeit somewhat smaller enhancement in the AMS reaction rate with temperature was observed for experiments conducted using platinum electrode. Platinum has very low overpotential for hydrogen evolution, therefore, it is possible that excessive proton reduction (equation 4) could lead to a relative decrease in the formate regeneration rate. All the studies [27-33] have advocated the suppression of hydrogen evolution for the reduction of bicarbonate ion to formate.



**Figure 12.** Influence of temperature on the extent of hydrogenation of AMS using graphite felt cathode (0.5 M formate, 10 % AMS in cyclohexane, 0.16 g/L of DDAB and 20 g/L Pd/g-Al<sub>2</sub>O<sub>3</sub>, pH =7, -1.4 V vs. SCE).

#### 4. CONCLUSION

This study has shown that it is possible to reduce  $\alpha$ -methyl styrene to cumene under mild reaction conditions using formate ions for shuttling hydrogens between the cathode of an electrochemical cell and the absorbed reactant on a catalyst. The main advantage of this process is that unlike the current commercial processes, molecular hydrogen gas under pressure is not required for AMS reduction to cumene.

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