



Electrocatalytic hydrogenation of phenol in aqueous solutions at a Raney nickel electrode in the presence of cationic surfactants

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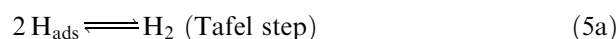
Abstract

The electrocatalytic hydrogenation (ECH) of phenol at a Raney nickel cathode was studied in aqueous solutions. At 30 °C, without surfactants, cyclohexanol was obtained with low or medium yields. The best results were observed in alkaline solutions (pH 9). At pH 2 the efficiency of the hydrogenation reaction is significantly improved by low amounts of didodecyltrimethylammonium bromide (DDAB). This surfactant effect is studied in relation to the substrate and hydrogen adsorption phenomena.

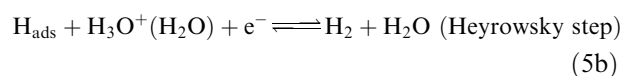
1. Introduction

The electrocatalytic hydrogenation (ECH) at Raney nickel (RaNi) cathodes constitutes a very convenient method that has been widely used for the hydrogenation of a variety of unsaturated compounds under mild conditions [1]. The chemisorbed hydrogen (H_{ads}) generated *in situ* by electroreduction of the hydronium ions (or water) (Reaction 1, Scheme 1) reacts with the adsorbed organic substrates ($Y = Z$) (Reactions 2–4) under normal pressure and low temperature (<100 °C). However, the competition between the substrate hydrogenation and the hydrogen evolution reaction (HER) (Reactions 5(a) and (b)) can drastically lower the current efficiency (CE) of the ECH and can even prevent the hydrogenation process.

The competition between ECH and HER depends on several factors [1]. Thus the use of aqueous electrolytes containing surfactants can favour the hydrogenation reaction. In particular, cationic surfactants strongly enhance the efficiency of the ECH of unsaturated compounds [2]. This results mainly from the incorporation of the organic substrate in a hydrophobic surfactant layer adsorbed on the cathode. The increase of the local substrate concentration on the catalyst favours the reaction with the adsorbed hydrogen. Thus the efficiency of the ECH at RaNi cathodes of carvone, limonene and *p*-menthene emulsified in aqueous solutions is markedly increased by the presence of low amounts of didodecyltrimethylammonium bromide (DDAB), a nonmicelle-forming surfactant that gives strong adsorptions at the interfaces [3].



Or



Scheme 1.

This paper reports the results of a study on the influence of cationic surfactants (especially DDAB) on the efficiency of the ECH of phenol to cyclohexanol in aqueous solutions at Raney Ni cathodes.

Cyclohexanol, an important industrial chemical product [4], can be obtained by the hydrogenation of phenol over different types of catalyst at elevated temperatures (180 to 275 °C) and various pressures (1 to 20 atm) [5–7]. ECH of phenol to cyclohexanone and cyclohexanol can be achieved under mild conditions (normal pressure and low temperatures (25–60 °C) ([8, 9] and ref. cited). The yields, the current efficiencies and the selectivity of the ECH depend on the nature of the catalyst. The best yields and current efficiencies are obtained with platinum and rhodium dispersed on carbon [8, 9]. On the

contrary in homogeneous solutions, without surfactants, RaNi gives poor yields and poor current efficiencies [10].

2. Experimental details

2.1. Reagents

Commercially available compounds were used as received: phenol (99%) from Prolabo, cyclohexanol (99%) and cyclohexanone (99.8%) from Aldrich, cetyltrimethylammonium bromide (CTAB) (99%) from Jansen Chemica, DDAB (99%) from Aldrich. Ethanol and water were distilled before use. Unless otherwise specified, the aqueous buffers were prepared as described in the 'Handbook of Chemistry and Physics' [11].

2.2. Electrodes

The RaNi cathodes used in electrosynthesis were prepared as already described [12] by codeposition on a stainless steel grid (3 cm × 4 cm) of nickel and of particles of Raney nickel alloy in a plating bath (constant current: 400 mA, amount of electricity: 1400 C for each side of the electrode). The percentage of the deposited alloy varied between 55 and 70% (this corresponds to 0.5–0.8 g RaNi catalyst after leaching). The electrodes used for the analytical studies (Tafel curves) were prepared by codeposition on one side of a nickel plate (1 cm × 1 cm), the other side being previously covered with an epoxy (Araldite). The current density and the amount of electricity were, respectively, 30 mA cm⁻² and 131 C. About 55 mg of Raney nickel alloy was deposited. Before use the electrodes were activated by leaching the aluminum in 30% aqueous NaOH (70 °C, 7 h).

2.3. Electrolysis

Electrolysis was carried out at 30 °C with a Tacussel PRT-100 potentiostat coupled to a Tacussel IG-5 LN coulometer. A two-compartment jacketed glass H-cell with a Nafion[®] 417 (Aldrich) membrane (7 cm²) was used. In the anodic compartment, the counter electrode, a platinum perforated cylinder (4 cm long × 3 cm dia.), was immersed in 100 ml of an aqueous solution of sulfuric acid (0.5 mol dm⁻³). The cathodic electrolytes consisted of aqueous buffers (100 ml) with or without surfactant. Some experiments were conducted in unbuffered aqueous solutions or in ethanol/water mixtures. The pH was controlled during electrolysis with Merk nonbleeding pH indicator strips (cf. [13] on pH measurements in the presence of surfactants). The potential was measured using an Ag/AgCl saturated KCl reference electrode (from Metrohm) (+197 mV vs NHE).

At the beginning of each experiment, prior to the addition of the substrate, the reduction of the electrolyte (hydrogen evolution) was done at constant current (100 mA). After the passage of 100 C the potential was

increased to the zero current point, its value varied between -0.5 V (acidic solutions) and -1 V (basic solutions). Then phenol was added in one portion (178 mg, 2 × 10⁻² mol dm⁻³ solution). This caused the reduction current to increase suddenly then decrease and stabilize. The low current densities (1.5–2 mA cm⁻²) thus obtained were kept constant during the electrolysis. In all experiments the theoretical amount of electricity (6 F mol⁻¹ of phenol) was consumed. The progress of the electrolysis was followed by gas-liquid chromatography (GLC) on a Varian 3300 chromatograph equipped with a FID detector and a C-R 6A Shimadzu integrator, using a DB-Wax fused silica capillary column (from J. & W. Scientific) (30 m, 0.5 μm). Aliquots (0.5 ml) from the catholyte were extracted with ether (after addition of 1 ml of saturated NaCl solution and acidification (pH ~1) with HCl). The products were identified by comparing their retention times with those of authentic samples (temperature programme: 80 °C (10 min)–160 °C (20 °C min⁻¹) (20 min)–220 °C (20 °C min⁻¹)). The yields and the mass balance were determined by the internal standard method (internal standard: *n*-heptadecane or *n*-dodecane (99%, Janssen Chemica)).

2.4. Products

The cathodic aqueous solutions were saturated with NaCl, acidified (pH ~ 1) with concentrated HCl and extracted (continuously in the case of micellar solutions) with ether. With hydro-organic solutions, prior to the extraction, ethanol was removed by distillation at atmospheric pressure and quantitatively analysed by GLC (the most of cyclohexanol distilled with ethanol). Quantitative analysis (yields and mass balance) was performed by GLC as indicated above. Then the ether was dried (MgSO₄), evaporated under vacuum and the mass balance was calculated from the weight of the crude product. In some experiments the crude product was also analysed by ¹H NMR spectroscopy (on a Bruker AM 300 spectrometer). A good fit was observed for the data obtained with these different analyses.

2.5. Polarization curves

Tafel curves were recorded in a one compartment Metrohm cell, with an Ag/AgCl saturated KCl reference electrode and a platinum wire as counter electrode. The measurements were performed using a Tacussel PJT-27 potentiostat, a Tacussel IMT-1 interface and a Voltmaster-2 Radiometer Analytical software. Several runs (6 to 10) were performed until a steady state was obtained.

2.6. Studies of phenol adsorption

These studies were carried out using solutions and cell identical to those used for the electrosynthesis. The

amount of phenol adsorbed on the cathode was estimated by the measure of the phenol concentration remaining in the bulk solutions. Aliquots (200 μl) were diluted in 10 ml aqueous buffer and the absorbance was recorded at 270 and 276 nm (on a Hewlett–Packard 8453 spectrophotometer). Phenol was entirely soluble in all buffers used.

3. Results and discussion

In all media used, with or without surfactant, no cyclohexanone was detected. Cyclohexanol was the sole product and its chemical yields (based on phenol) correspond also to the current efficiencies, since in all experiments the theoretical amount (6 faraday mol^{-1}) of electricity was consumed. As previously pointed out by Martel et al. [10] the absence of cyclohexanone indicates that its ECH on RaNi is faster than that of phenol.

3.1. ECH in the absence of surfactants

Since the sole processes occurring are hydrogenation (Reactions 2–4, Scheme 1) and hydrogen evolution (Reactions 5), the current efficiency (CE) is a measure of the competition between the two processes. Their relative rates depend on the strength of the bond to be hydrogenated and on the different factors that influence the adsorption phenomena and the activity of chemisorbed hydrogen ([1] and references cited therein). For a given electrode, among these factors, the pH of the solution, the organic cosolvent, and the supporting electrolyte can influence the efficiency of the ECH reaction [1, 12, 14–16]. Therefore ECH of phenol has been performed at 30 °C in different acidic or alkaline solutions. Several main points can be drawn from the results recorded in Table 1.

In acidic solutions (Table 1, entries 1–5), and in agreement with the results previously published by Martel et al. [10], poor yields and poor current efficiencies were observed in the different electrolytes.

At pH 2, the best CE (27%) was obtained in the buffer HCl/KCl (Table 1, entry 1). The use of sodium hydrogen sulfate as supporting electrolyte (Table 1, entry 2) led only to a slight decrease of the ECH efficiency (CE 21%).

A more pronounced inhibition (CE 15%) was observed in a slightly acidic solution in the presence of boric acid (Table 1, entry 3). A similar effect was also reported by Martel et al. for the ECH of phenol on RaNi in the same electrolyte [10].

An important decrease of the ECH efficiency (CE 6%) was also observed when the buffer was made of an organic acid/base couple (entry 4). As pointed out by Lessard and coworkers [12] this could result from the adsorption of the carboxylic acid, which could be strong enough to displace the phenol. Likewise, a competitive adsorption was previously put forward to explain the decrease in catalyst activity due to an organic cosolvent [12, 17]. A similar inhibition occurred in our experimental conditions in the presence of 50% of ethanol as shown by the very low yield value (CE <1%, entry 5) (obtained from glc analysis of distilled ethanol). In the presence of ethanol, the material balance is lower (80%, entry 5) than those observed in aqueous solutions (90–93%, entries 1–4). Nevertheless, assuming that cyclohexanol is the sole compound lost, its yield (~10%), recalculated for a mass balance similar to those of entries 1–4, remains lower than the yields observed in the absence of ethanol (entries 1–3).

The ECH reaction was more efficient in an alkaline solution than in the acidic or neutral ones. At pH 9 the yield of cyclohexanol (42%) (Table 1, entry 6) was significantly higher than that at pH 2 (21–27%). This result is in agreement with the kinetic studies of the catalytic hydrogenation of phenol over Pd/C and Pd black catalysts in aqueous media previously published by Wismeijer and coworkers: the rate of hydrogenation of phenol increases with the pH, and reaches a maximum at a pH between 8 and 10, because of the higher rate of hydrogenation of phenolate anion with respect to phenol [18].

Table 1. ECH of phenol (2×10^{-2} mol dm^{-3}) at 30 °C, in aqueous solutions, on RaNi: effect of electrolytes, pH, and cosolvent
Experimental conditions: constant current densities: 1.7 mA cm^{-2} , cathodic potential: -0.6 V to -1 V vs Ag/AgCl, $Q = 6$ faraday mol^{-1}

Entry	Solution	pH (initial–final)	Unreacted phenol* /%	Cyclohexanol: yield* and current efficiency† /%	Material balance* /%
1	Buffer‡ HCl/KCl	2.0–3.5	65§	27§	92§
2	NaHSO ₄ 0.1 M H ₂ SO ₄ 5×10^{-3} M	2.0–4.0	69	21	90
3	H ₃ BO ₃ 0.5 M NaCl 0.05 M	4.5–6.0	75	15	90
4	Buffer** Citrate/HCl	2.0–2.0	87	6	93
5	Buffer (HCl/KCl) EtOH (50/50)	2.0–2.0	80	<1	80
6	Buffer** H ₃ BO ₃ /NaOH/KCl	9.0–10.0	43	42	85

* Determined by GLC.

† Cyclohexanol was the sole product and the theoretical amount of electricity was used; therefore yields and current efficiencies have the same numerical values.

‡ HCl 0.04 M, KCl 0.16 M [11].

§ Quantitative analyses by GLC and ¹H NMR.

** Titrisol Merck.

Taking into account these observations, the studies of the influence of surfactants on the phenol ECH reaction were realized at pH 2 and 9 in inorganic buffers without organic cosolvents.

3.2. ECH in the presence of surfactants

Numerous publications concern the use of surfactants in electrochemistry both in analytical studies and in electrosyntheses. A surfactant can influence an electrochemical process both by its adsorption on the electrodes and by the formation microheterogeneous systems (micelles, microemulsions, bicontinuous microemulsions, etc). Electrochemistry and electrochemical catalysis in the presence surfactants (i.e., in microheterogeneous solutions) has been the subject of several recent reviews [19–23]. The modification of the electrode surface by the surfactant adsorption and the solubilization equilibria between the aqueous electrolyte and the micellar (or microemulsified) pseudo-phase represent two important parameters. As mentioned in the introduction we reported earlier that cationic surfactants could favor hydrogenation over hydrogen desorption [2, 3]. Soluble cationic surfactants like cetyltrimethylammonium bromide (CTAB) lead to the formation of micelles when their concentration exceeds the critical micellar concentration (CMC). Therefore, both solubilization equilibria and adsorption phenomena take place. On the contrary, less soluble surfactants with two tails like didodecyldimethylammonium bromide (DDAB) give essentially strong adsorptions at the interfaces even at very low concentrations. In this case, the modification of the electrode surface represents the main parameter.

The influence on the ECH of phenol of the two types of surfactant (namely CTAB and DDAB) is presented below.

3.2.1. ECH of phenol in cationic micellar solutions

The current efficiencies and the percentage of unreacted phenol obtained at pH 2 ($\text{H}_2\text{SO}_4/\text{NaHSO}_4$ electrolyte) with increasing concentrations of CTAB are recorded in Table 2. Figure 1 shows the variation of CE as a function of CTAB concentration.

When the concentration of CTAB rises a poor catalytic effect is obtained: the current efficiency increases only from 21% to 31% (Table 2, entries 1–4) and then decreases (Figure 1). A similar behavior was observed with this surfactant in the case of ECH of limonene and carvone in aqueous electrolytes [2], but with these two substrates the improvement of the hydrogenation reaction was much higher than that observed with phenol in this work. Moreover, in some experiments, it was difficult to obtain a good material balance (e.g., entries 5 and 7, Table 2) (some loss of organic compounds, due to the association with the micelles, occurred during the work up). Therefore, taking account of the very low catalytic effect, the

Table 2. ECH at 30 °C of phenol ($2 \times 10^{-2} \text{ mol dm}^{-3}$) in aqueous solutions, pH 2 (NaHSO_4 0.1 mol dm^{-3} , H_2SO_4 $5 \times 10^{-3} \text{ mol dm}^{-3}$) on RaNi: influence of CTAB concentration
Electrolysis conditions: see Table 1

Entry	[CTAB] / mol dm^{-3}	Unreacted phenol* / %	Current efficiency* / %	Material balance* / %
1	0	69	21	90
2	5.5×10^{-4}	60	20	80
3	1.37×10^{-3}	67	31	98
4	2.1×10^{-3}	59	31	90
5	2.75×10^{-3}	50	27	77
6	5.5×10^{-3}	72	20	92
7	1.4×10^{-2}	64	11	75

* Determined by GLC.

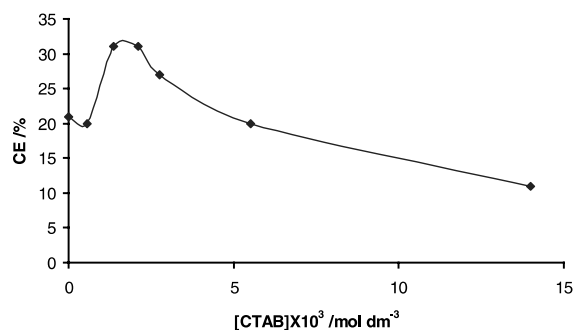


Fig. 1. Current efficiencies for phenol ECH at pH 2 as a function of CTAB concentration.

ECH of phenol in cationic micelles was not studied in detail.

3.2.2. ECH of phenol in aqueous solutions in the presence of DDAB

The influence of DDAB concentration on the efficiency of the ECH of phenol was studied both at pH 2 (HCl/KCl solutions, cf. footnote Table 1) and 9 ($\text{H}_3\text{BO}_3/\text{NaOH}/\text{KCl}$, cf. footnote Table 1). The results obtained at 30 °C after the consumption of the theoretical amount of electricity are recorded in Tables 3 (pH 9) and 4 (pH 2).

The following main points can be drawn from these results:

- (i) In alkaline solution the ECH of phenol is less efficient in the presence of surfactant in the whole range of concentrations used. The CE drops from 42% (Table 3, entry 1) to values close to 30% (Table 3, entries 2–6), respectively, in the absence and in the presence of DDAB as shown in Figure 2 (curve 2).
- (ii) In acidic solutions, as the DDAB concentration increases from 0 to $2.2 \times 10^{-4} \text{ mol dm}^{-3}$ (Table 4, entries 1–5) the CE grows up from 27% to a good value (77%) (entry 5) and then sharply drops for higher surfactant concentrations (Table 4, entries 8–11) (Figure 2, curve 1). Thus, a very low DDAB

Table 3. ECH of phenol (2×10^{-2} mol dm $^{-3}$) in aqueous solutions, at 30 °C, pH 9*, on RaNi: influence of DDAB concentration

Electrolysis conditions: see Table 1 (cathodic potential: -1 V vs Ag/AgCl)

Entry	[DDAB] /mol dm $^{-3}$	Unreacted phenol† /%	Current efficiency† /%	Material balance† /%
1	0	41	42	83
2	6.5×10^{-5}	65	28	93
3	2.16×10^{-4}	61	29	90
4	4.32×10^{-4}	50	30	80
5	8.64×10^{-4}	67	23	90
6	4.32×10^{-3}	43	34	77

* H $_3$ BO $_3$ /NaOH/KCl (Titrisol Merck).

† Determined by GLC.

Table 4. ECH of phenol (2×10^{-2} mol dm $^{-3}$) in aqueous solutions, at 30 °C, pH 2*, on RaNi: influence of DDAB concentration

Electrolysis conditions: see Table 1

Entry	[DDAB] /mol dm $^{-3}$	Unreacted phenol† /%	Current efficiency† /%	Material balance† /%
1	0	70‡	27‡	97‡
2	2.7×10^{-5}	56	28	84
3	5.4×10^{-5}	52‡	36‡	88‡
4	1.08×10^{-4}	56	41	97
5	2.16×10^{-4}	21‡	77‡	95‡
6	2.16×10^{-4}	29	60	89
7	2.16×10^{-4}	45‡,§	60‡,§	95‡,§
8	5.4×10^{-4}	49	45	94
9	2.16×10^{-3}	43	46	89
10	5.4×10^{-3}	43	41	84
11	8.65×10^{-3}	58‡	20‡	78‡

* HCl 0.04 M, KCl 0.16 M [11].

† Determined by GLC.

‡ Quantitative analyses by GLC and 1 H NMR.

§ [phenol] = 4×10^{-2} mol dm $^{-3}$.

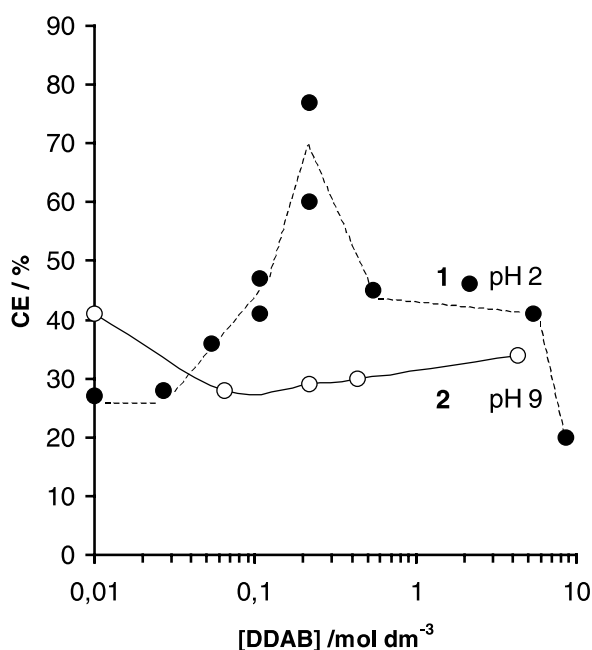


Fig. 2. Current efficiencies for phenol (2×10^{-2} mol dm $^{-3}$) ECH as a function of DDAB concentration. Electrolysis conditions: see footnotes in Tables 1 and 3.

concentration ($\sim 2 \times 10^{-4}$ mol dm $^{-3}$), 100 times lower than that of the substrate (2×10^{-2} mol dm $^{-3}$), induces a strong improvement of the efficiency of the hydrogenation. Some variations of CE have been observed, in particular in the narrow range of DDAB concentrations leading to the highest hydrogenation efficiency. Thus, CE values vary between 60–77% (Table 4, entries 5 and 6) in the presence of 2.16×10^{-4} mol dm $^{-3}$ of DDAB. This could result from differences in the electrode surface state (cf. the discussion below). Taking these variations into account, and in agreement with our previous studies on the ECH of limonene and carvone [2, 3], the surfactant/substrate ratio has no significant influence on the hydrogenation efficiency. Indeed similar CE values were obtained with 2×10^{-2} and 4×10^{-2} mol dm $^{-3}$ of phenol

concentrations at the optimum DDAB concentration (Table 4, entries 5–7).

The large increase in the efficiency of the ECH of phenol occurring at pH 2 (Figure 2, curve 1) presents an analogy with the catalytic effect previously observed for the ECH of limonene in the presence of DDAB [3]. With both substrates, the maximum improvement of the hydrogenation is obtained for low surfactant concentrations (close to 2×10^{-4} mol dm $^{-3}$ in both cases). However, the ECH of phenol and limonene differs on two main points. First, the sharp decrease of the CE of the ECH of phenol beyond the optimum surfactant concentration does not take place with limonene. The overall chemical yield (and CE) of *p*-menthene and *p*-menthane obtained by ECH of limonene remains nearly constant ($82 \pm 8\%$) upon increasing the DDAB concentration further [3]. Secondly, the hydrogenation of phenol is slightly inhibited by the DDAB at pH 9, whereas that of limonene is strongly enhanced at pH 10. These differences suggest that the way in which DDAB influence the competition between ECH and HER could be different in these two cases.

The hydrogenation reaction occurs between adsorbed species (Reaction 3, Scheme 1) and depends on the surface coverage by the adsorbed organic substrate and by the adsorbed hydrogen (respectively Θ_{Sub} and Θ_{H}). As previously reported [1], the rate of this reaction is given as

$$v = k^a \Theta_{\text{Sub}} (\Theta_{\text{H}})^x$$

where k^a is the surface rate constant and x the reaction order with respect to the adsorbed hydrogen (cf. [1]). The different limiting cases in relation to the adsorption phenomena are described in [1]. In particular, in the presence of fast and strong adsorption of the organic substrate, the rate of the ECH reaction is maximal for

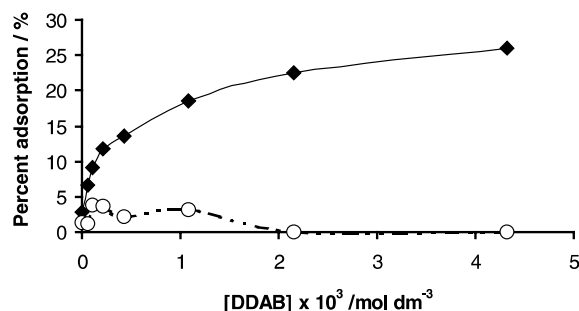


Fig. 3. Percentage of phenol adsorbed at the interfaces as a function of DDAB concentration. Key: (◆) pH 9; (○) pH 2.

the higher value of the product $\Theta_{\text{Sub}}\Theta_{\text{H}}$ [1]. Thus the improvement of the ECH of limonene obtained in the presence of small amounts of DDAB corresponds to a very significant adsorption of the organic compounds (more than 90% of limonene and reaction products are adsorbed on the cathode) [3]. In this work the adsorption of phenol was estimated from measurements of its concentration in the reaction medium (see Section 2). Figure 3 shows the percentage of adsorbed phenol as a function of DDAB concentration. At pH 2 and 9 the adsorption is very low in the absence of surfactant (<3%). It increases in alkaline electrolyte with the amount of DDAB and reaches a maximum value close to 25%. In contrast in acidic solution the adsorption of phenol is always lower than 4% for all DDAB concentrations. The striking difference of adsorption in alkaline and acidic solutions indicates an association between phenol and the surfactant layer on the cathode which is higher at pH 9 than at pH 2. This may result from the electrostatic interaction between the cationic DDAB head group and the phenate anions which occurs only in alkaline solutions.

Moreover, neither the poor phenol adsorption in acidic solution nor its medium value under basic conditions can explain the improvement and the slight inhibition of the ECH reaction observed, respectively, at pH 2 and 9. In other words the observed variations of the competition between hydrogen evolution (Reaction 5(a) and (b), Scheme 1) and hydrogenation reaction (Reaction 3, Scheme 1) cannot be correlated with the parameter Θ_{Sub} .

The second parameter Θ_{H} depends on the formation, the evolution and the consumption (in ECH processes) of hydrogen, which can be studied by means of Tafel curves. The theoretical and experimental aspects in this field were previously developed by Lasia and coworkers, who investigated the influence of organic compounds on hydrogen formation and evolution [1, 24]. The general character of the steady-state polarization curves obtained in our experimental conditions was similar in the different media used in this work.

In the absence of surfactant, a shift of the equilibrium potential toward positive values is observed, at pH 2 and 9, on addition of phenol. This behavior is similar to that previously observed with cinnamic acid by Lasia et al.

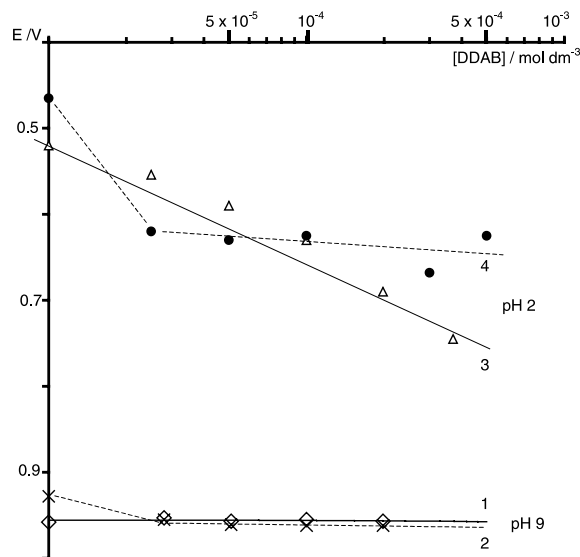


Fig. 4. Variation of the open-circuit potential as a function of DDAB concentration. Solid lines (curves 1 and 3): aqueous buffer without phenol. Dotted lines (curves 2 and 4): aqueous buffer with phenol (2×10^{-2} mol dm⁻³).

[24]. It is consistent with a weak and fast adsorption of the organic substrate [1].

The effect of DDAB on the polarization curves depends on the pH of the solution as shown by the values of the open-circuit potential (i.e., the minimum on the Tafel plots) recorded in Figure 4 as a function of DDAB concentration. In alkaline buffer, taking into account the experimental errors, a similar behaviour is observed with and without phenol, (respectively curves 2 and 1, Figure 4). The minimum on the steady-state polarization curves remains constant for the whole range of surfactant concentration. Thus DDAB has no (or very little) influence on Θ_{H} . In acidic buffer, in the absence of phenol, the increase in surfactant concentration leads to a shift of the equilibrium potential toward negative values (Figure 4, curve 3) without significant modification of the current. This suggests an increase in surface coverage by adsorbed hydrogen which may lead to the improvement in the efficiency of the phenol ECH reaction observed at pH 2 with DDAB. In the presence of the organic compound (Figure 4, curve 4) the shift of potential is less pronounced as a consequence of the hydrogenation process.

In conclusion, the increase of the Θ_{H} values at pH 2 can explain, at least partially, the catalytic effect of DDAB. At pH 9, the absence of a surfactant effect on the equilibrium potential, that is, on Θ_{H} , is in agreement with the absence of a catalytic effect of the surfactant. Moreover, the whole set of data obtained in alkaline solution in the presence of DDAB (slight inhibition effect and increase of Θ_{Sub} without modification of Θ_{H}) suggests phenol adsorption on noncatalytic sites such as the Al^{3+} cations of Al_2O_3 . Indeed, alumina formed during the lixiviation is present in the Raney nickel catalyst [25] and also on RaNi cathodes [26]. Moreover,

a strong adsorption of phenate anions on Al_2O_3 has also been previously demonstrated [27].

4. Conclusions

The poor yields and current efficiencies obtained for the ECH of phenol in aqueous solutions at Raney nickel cathodes can be improved by the presence of low amounts of DDAB in acidic medium. Thus, high current efficiencies (close to 80%) can be obtained.

The catalytic effect of DDAB is mainly due to an increase of the surface coverage by adsorbed hydrogen (i.e., a decrease of the competitive hydrogen evolution reaction) and not from an increase of the substrate adsorption.

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