EFFECT OF TRITON X-100 ON THE ELECTROCHEMICAL REDUCTION OF N-METHYLNICOTINIC ACID AT A MERCURY ELECTRODE

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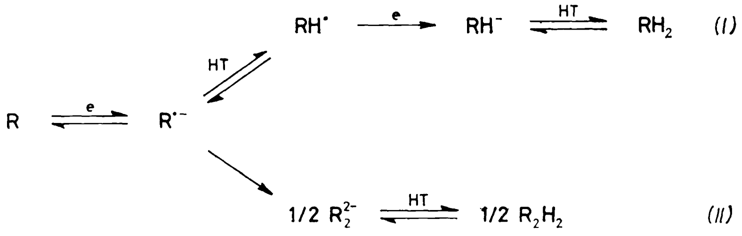
Dedicated to the memory of Prof. J. Heyrovský on the occasion of his centenary.

Reaction mechanism for pH ranges below and above 7·5 has been formulated. Theoretical *i–E–c–t* relationship has been proposed and discussed on the basis of the experimental results.

The influence of strong surfactants such as Triton X-100 on the electrohydrodimerization of activated olefins (diethyl fumarate, fumarodinitrile and ethyl cinnamate) and α,β-unsaturated carbonyl compounds (chalcone) was studied by Guidelli et al.[1-4].

The reduction of activated olefins in aqueous media yields either the saturated monomer or the dimer:



In the absence of strong surfactants, the reduction yields the saturated monomer, RH_2, (mechanism (*I*)), since water molecules adsorbed on the negatively charged electrode are proton donors strong enough to favour the step involving the protonation of $R^{\bullet -}$ and hence the formation of the saturated monomer preferentially to the parallel pathway yielding the hydrodimer, R_2^{2-} or R_2H_2, (mechanism (*II*)). On the contrary, bulk water molecules are practically ineffective in this respect.

The role of strong surfactants such as Triton X-100, which displaces adsorbed

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water molecules completely upon direct contact with the electrode and hence deactivate the heterogeneous protonation of $R^{\bullet -}$ (ref.[5]), is therefore essential to favour the electrohydrodimerization of these activated olefins.

However, chalcone yields a one-electron wave due to the hydrodimer formation (R_2H_2), even in aqueous media containing no surfactant. This is not surprising since the neutral radical of chalcone ($RH^{\bullet}$), whether it results from the heterogeneous protonation of the anion radical by adsorbed water molecules or from the homogeneous protonation by some proton donor, tends to dimerize. In this respect, the effect exerted by Triton X-100 upon chalcone reduction in aqueous media is less significant than that it exerts upon the reduction of the above-mentioned deactivated olefins. However, Triton X-100, by inhibiting chalcone specific adsorption, deactivates the heterogeneous pathway in favour of the homogeneous one.

This singular behaviour of chalcone can be ascribed to its α,β-unsaturated carbonyl nature since the anion radicals of these compounds are more liable to accept a proton on the oxygen rather than the carbon atom and acquire a certain degree of conjugation, which favours its stabilization by resonance. Conversely, the anion radicals of activated olefins are protonated on the carbon atom and have a greater tendency to be electroreduced to the saturated monomer than to dimerize.

On the other hand, in previous work[6], we showed Triton X-100 to inhibit the electrohydrodimerization of nicotinic acid between pH 2 and 4. Thus, the two one-electron waves observed in these media (the first of which is due to the electrohydrodimerization) decrease with increasing Triton concentration (particularly the first) to the point that only one reduction wave, with the typical features of that yielded by a two-electron process, is obtained at Triton concentrations above $1 . 10^{-4}$ mol l^{-1}.

The aim of this work was to study the effect of Triton X-100 on the electrochemical reduction of N-methyl nicotinic acid in aqueous solutions over a wide pH range.

EXPERIMENTAL

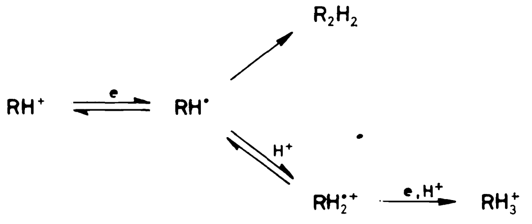
Triton X-100 was Merck a.g. and was employed at a concentration of $1 \cdot 10^{-4}$ mol l^{-1}. All other experimental conditions are described in ref.[7].

RESULTS AND DISCUSSION

Acid Medium (pH < 4)

In previous work we studied the electrochemical behaviour of N-methyl nicotinic acid in aqueous solutions[7] and found that, in acid media, the first reduction wave was somewhat atypical since its features were consistent with neither those of an electrohydrodimerization process nor those of the formation of the saturated monomer.

We put forward a reaction mechanism accounting for the value of the limiting current, the variations of i_L with the reactant concentration and the pH over the range 2–4, and the voltammetric peak due to the oxidation of the dimer yielded in the reduction scan. The mechanism was:



However, the presence of Triton X-100 introduces major changes. First, the variation of i_L with c is linear, at least at concentrations below $1 \cdot 10^{-3}$ mol l^{-1} (Fig. 1). Second, the limiting current remains constant over the pH range 2–4 (Fig. 2). Third, no oxidation peak is observed by cyclic voltammetry. Finally, the half-wave potential is independent of the drop time and the log i_L vs log t plot is linear, with a slope of 0·30.

These variations are typical of an irreversible two-electron wave with a slight kinetic character, yielding a saturated monomer.

These results clearly indicate that the adsorption of Triton X-100 on the electrode surface inhibits the competition between the one- and two-electron processes, of which only the latter occurs:

$$RH^+ \overset{e}{\rightleftharpoons} RH^\bullet \overset{H^+}{\rightleftharpoons} RH_2^{\bullet +} \xrightarrow{e,H^+} RH_3^+ .$$

The reduction process is quite simple in this instance; the variations of i_L with the

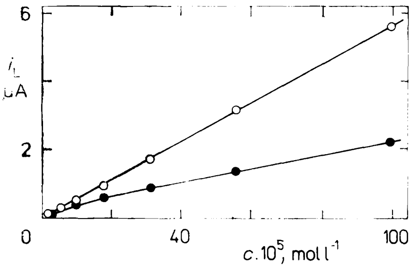


Fig. 1

Variation of i_L with c, pH 1.8: ● without Triton X-100; ○ with $1 \cdot 10^{-4}$M Triton X-100

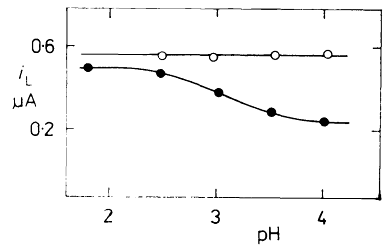


Fig. 2

Variation of i_L with pH: ● without Triton X-100; ○ with $1 \cdot 10^{-4}$M Triton X-100 reactant concentration and pH are "normal", i.e. vary linearly and the reduction to the saturated monomer is irreversible, so no oxidation peak is observed by cyclic voltammetry.

The independence of $E_{1/2}$ with t confirms this conclusion. Moreover, the fact that the height of the wave is a little over twice of that corresponding to a one-electron process governed by diffusion and the slope of the log i_L vs log t plot, clearly indicate that the dehydration and reduction of the aldehyde (RH_3^+) take place to some extension. This is logical since the estimated half-life of the hydrated aldehyde is approximately 7 s (ref.[8]), i.e. of the same order as the electrolysis time in dc polarography, and the reduction of the resultant carbonyl group takes place at potentials less negative than that of the carboxyl group[9].

Neutral and Basic Media (pH > 4)

Above pH 4, the effect of Triton X-100 on the electrochemical behaviour of N-methyl nicotinic acid is smaller than in acid media.

We carried out a logarithmic analysis of the reduction wave by plotting E vs $\log [2^{a-b}(i_L - i)^a / i^b i_L^{a-b}]$ (ref.[10]). The only differences observed lie in the fact that in the logarithmic analysis, the experimental data do fit the equation corresponding to $a = 1$ and $b = 2/3$ instead of that corresponding to $a = 4/3$ and $b = 2/3$ (in the absence of Triton), and the slope of the $E_{1/2}$ vs $\log c$ plot and the reaction order with respect to the reactant are 21 mV and 1·5, respectively. Apart from this, all data are identical with those obtained for aqueous solutions containing no Triton.

These results indicate a change in the dimerization mechanism which proceeds via radical-radical coupling in the reaction layer rather than through radical-substrate coupling in the reaction layer[10].

TABLE I

Comparison of the theoretical and experimental results

Slopes and reaction orders	Theoretical	Experimental
Tomes slope, mV	59·2	60
$\partial E_{1/2}/\partial \mathrm{pH}$ for pH < 7·5	−59·2	−60
for pH > 7·5	0	0
$\partial E_{1/2}/\partial \log t$	19·7	18
$\partial E_{1/2}/\partial \log c$	19·7	21
Tafel slope, mV	−39·4	−40
order with respect to H^+ ion		
pH < 7·5	1·5	1·5
pH > 7·5	0	0
order with respect to reactant	1·5	1·5

According to the above-mentioned results, and taking into account that N-methyl nicotinic acid occurs as a zwitterion above pH 2, (ref.[9]), the reaction mechanism can be formulated as follows:

Below pH 7·5

$$\begin{array}{rcl} R^{\pm} + e & \rightleftarrows & R^{\bullet -} \\ R^{\bullet -} + H^{+} & \rightleftarrows & RH^{\bullet} \\ 2\,RH^{\bullet} & \rightarrow & R_2H_2 \end{array}$$

and above pH 7·5

$$\begin{array}{rcl} R^{\pm} + e & \rightleftarrows & R^{\bullet -} \\ 2\,R^{\bullet -} & \rightarrow & R_2^{2-}\,, \end{array}$$

where the rds would occur in the reaction layer.

The theoretical i–E–c–t relationship corresponding to these schemes[10] is:

$$E = E_0 + \frac{RT}{F} \ln \frac{2^{1/3}(i_L - i)}{i_L^{1/3} i^{2/3}} + \frac{RT}{3F} \ln K f(c_H)\, c^2 t\,,$$

where K is a constant and $f(c_H)$ is equal to c_H^2 at pH $< 7{\cdot}5$ and 1 at pH $> 7{\cdot}5$.

Table I compares the theoretical values of the slopes and reaction orders derived from this equation with the experimental results.

As can be seen, the two sets are quite consistent.

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