

Ultrasound-assisted electrochemical reduction of emulsions in aqueous media

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The electrochemical reduction of diethylmaleate, diethylfumarate and diethylacetylene dicarboxylate in the form of microscopic droplets generated by applying power ultrasound to aqueous electrolyte media allows a clean hydrogenation of the carbon-carbon double/triple bond whilst providing a novel and versatile methodology for electrochemistry of insoluble materials in aqueous environments.

In terms of practical applications water can be regarded as an ideal reaction environment for organic electrochemical processes with good conductivity and polarity, stabilizing effects on radical intermediates, and straightforward product isolation by extraction or filtration.¹ Further it is preferable to organic solvents on environmental grounds. Therefore the extension of the range of systems undergoing electrochemical transformations in water is of considerable interest and studies employing surfactant-stabilized emulsions and suspensions have been described.²

Ultrasound emitted by a horn source situated in a conventional electrochemical cell³ allows the formation of emulsions without stabilizing agents simply by mechanical forces which arise at the liquid/liquid phase boundaries.⁴ In this study it is demonstrated how this novel experimental approach allows direct voltammetry and electrolysis in aqueous media of materials hitherto thought to be essentially insoluble.

A thermostatted electrochemical cell equipped with an ultrasonic horn probe as shown in Fig. 1 can be used for the study of sonoelectrochemical processes.³ The cell which has recently been used in the study of homogeneous systems⁵ may be used without further modification for voltammetric and bulk electrolysis experiments with emulsions. In Fig. 2 voltammograms obtained for the reduction of emulsions[†] of diethylfumarate, diethylmaleate and cyclohex-2-en-1-one in aqueous 1.0 M MgCl₂ at a 3 mm diameter glassy carbon disc electrode are shown. For diethylfumarate a well defined response for the reduction process at $E_{1/2} = -1.16$ V vs. SCE can be observed.

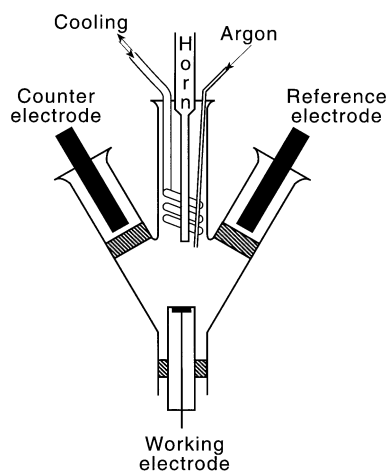


Fig. 1 Schematic drawing of the thermostatted small volume (20 ml) sonoelectrochemical cell employed for sonovoltammetric and electrolysis experiments

The response is sigmoidally shaped and therefore well behaved even at the very high rates of mass transport applied in the presence of ultrasound. For homogeneous solutions the rate of mass transport⁵ is related to the diffusion layer thickness, δ , and the diffusion coefficient, D [eqn. (1)].

$$I_{\text{lim}} = \frac{nFDAc_{\text{total}}}{\delta} \quad (1)$$

In the following we use this equation to quantify the rates of mass transport and for two-phase systems we report 'apparent diffusion coefficients', D_{app} , which have no direct physical significance other than allowing comparison with homogeneous conditions. For the reduction process described here the additional parameters in eqn. (1) are the number of transferred electrons, $n = 2$ (*vide infra*), the Faraday constant, F , the electrode area, $A = 7.06 \times 10^{-6}$ m², the total concentration, c_{total} , and the observed limiting current, I_{lim} . The determined apparent diffusivity for diethylfumarate, $D_{\text{app}} = 0.58 \times 10^{-9}$ m² s⁻¹, is somewhat smaller than the one estimated⁶ for the hypothetical case of diethylfumarate dissolved homogeneously in water (Table 1), but is still rather large and sufficient for bulk electrolysis purposes. The physicochemical meaning of the observed magnitude of the limiting currents is more complex and determined either by parameters such as the rate of dissolution, the size of the microdroplets, and the approach distance between microdroplets and the electrode surface or a 'wetting' process.¹ Nevertheless, the magnitude of the D_{app} values suggests the ability of ultrasound to assist the electrolysis of insoluble materials at efficiencies approaching those that would be accomplished if the substrates were soluble.

For the reduction of diethylfumarate at a glassy carbon electrode the Tomès criterion, $E_{3/4} - E_{1/4} = 80$ mV, suggests an overall fast and in the electrochemical sense almost reversible

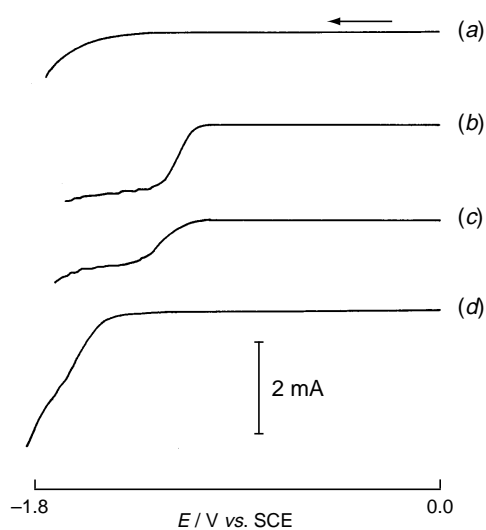


Fig. 2 Voltammograms obtained for the reduction of 10 μ l diethylfumarate (b), diethylmaleate (c), and cyclohex-2-en-1-one (d) emulsified in 20 ml 1.0 M aqueous MgCl₂ [(a) background] at a 3 mm diameter glassy carbon electrode (25 °C, 150 W cm⁻², scan rate 0.1 V s⁻¹)

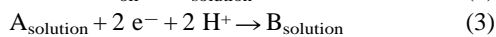
Table 1 Sonovoltammetric data^a for the reduction of 10 μl insoluble organic compound emulsified in 20 ml aqueous 1.0 M MgCl_2 in the presence of 150 W cm^{-2} ultrasound

| Compound | $E_{1/2}/$ V vs. SCE | n | $10^3 c_{\text{total}}/$ M | $I_{\text{lim}}/$ μA | $10^9 D_{\text{sol}}^b/$ $\text{m}^2 \text{s}^{-1}$ | $10^9 D_{\text{app}}^c/$ $\text{m}^2 \text{s}^{-1}$ |
|-----------------------------------|-------------------------|-----|-------------------------------|------------------------------------|--|--|
| Diethylfumarate | -1.16 | 2 | 3.0 | 1500 | 0.61 | 0.58 |
| Dimethylmaleate | -1.34 | 2 | 4.0 | 2500 | 0.73 | 0.73 |
| Diethylmaleate | -1.23 | 2 | 3.1 | 1050 | 0.61 | 0.39 |
| Dibutylmaleate | -1.24 | 2 | 2.2 | 180 | 0.50 | 0.09 |
| Diethylacetylene dicarboxylate | -1.28 | 4 | 3.0 | ca. 500 | 0.60 | 0.20 |
| Cyclohex-2-en-1-one | -1.58 | 2 | 5.2 | ca. 1700 | 0.83 | 0.38 |

^a Voltammograms obtained at 25 $^\circ\text{C}$, scan rate 0.1 V s^{-1} , at a 3 mm diameter glassy carbon disc electrode. $E_{1/2}$ corresponds to the half wave potential for sigmoidal responses. ^b An empirical expression introduced by Wilke and Chang allows the diffusivity, D_{sol} , to be estimated to within $\pm 10\%$ accuracy. ^c The apparent diffusivity D_{app} has been calculated assuming a homogeneous solution based on eqn. (1) and using the approximate diffusion layer thickness $\delta = 1.6 \mu\text{m}$.⁵

electrode process. In the case of diethylmaleate at $E_{1/2} = -1.23$ V vs. SCE also a well defined response can be observed, although now the voltammetric wave is more drawn out ($E_{3/4} - E_{1/4} = 100$ mV). For comparison, the electrochemical reduction of diethylmaleate dissolved in *N,N*-dimethylformamide described by Bard *et al.*⁷ involves the *cis-trans* isomerization of the radical anion formed as a short-lived intermediate in the vicinity of the electrode surface. It was also shown that in *N,N*-dimethylformamide solution the reduction of diethylmaleate occurs at potentials approximately 0.2 V more negative of those for the reduction of the fumarate. In regard of the contrasting voltammetric features in water and in organic media, for the reduction of diethylmaleate in aqueous media an extremely fast rate of the *cis-trans* isomerization possibly due to the solvent polarity may be predicted.

The comparison of the electrochemical reduction of dimethyl-, diethyl-, and dibutyl-maleate emulsions in aqueous 1.0 M MgCl_2 demonstrates the effect of the substrate solubility on the cathodic limiting currents (Table 1). The increase in the chain length of the carbon residue significantly alters the magnitude of the apparent diffusivity in agreement with the mechanism generally applied¹ for electrochemical processes in emulsion systems [eqn. (2)–(4)].



Under ultrasound condition the oil microdroplets penetrate into the Nernst diffusion layer at the electrode surface and act as a local source of the depolarizer [eqn. (2)]. After the product, B_{solution} , has been generated at the electrode surface the reaction step (4) is essential for maintaining an active electrode surface by re-absorbing the product. Depending on the kinetic regime of the process the equilibrium concentration of the depolarizer in the aqueous electrolyte or the rate of dissolution in step (2) govern the limiting current.

In order to analyse the nature of the observed reduction process bulk electrolyses[‡] of diethylfumarate, diethylmaleate, and diethylacetylene dicarboxylate emulsified in aqueous 1.0 M MgCl_2 were performed. The reduction of emulsions of diethylfumarate and -maleate assisted by additives and special hydrophobic electrodes in the absence of ultrasound has been reported recently⁸ by Nonaka and coworkers. Not surprisingly, the scale-up of the sonoelectrochemical process involves a non-simple dependence of the observed limiting current for the reduction reaction on the amount of reactant present. On glassy carbon electrodes a tenfold increase in the amount of organic phase resulted in sonovoltammetric responses with decaying limiting currents characteristic for electrode-blocking processes. However, a clean reduction process at a large surface area gold electrode following a two-electron–two-proton reaction pathway with reduction of the alkenic double bond was

observed for diethyl-fumarate and -maleate. Due to the more negative reduction potential diethylacetylene dicarboxylate is reduced directly in a $4e^-$ process to diethylsuccinate. After passing two- to three-fold excess charge the products were isolated by simple extraction with chloroform and analysed by NMR spectroscopy. Yields of the isolated compounds are typically 50–70% based on the starting material and increase with the amount of charge passed. Side-products due to processes such as hydrodimerization or polymerization have not been observed. The process responsible for the loss of faradaic efficiency appears to be hydrogen evolution.

Although details of the mechanism for sonoelectrochemical redox processes in emulsions remain to be studied, it is clear that the effect of ultrasound, to generate microscopically small droplets whilst ensuring extremely high rates of mass transport, considerably extends and facilitates the possibilities in emulsion electrochemistry.

Footnotes

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† The ultrasound generator employed was a VCX400 model sonic horn (Sonics and Materials, USA) equipped with a stepped titanium microtip (electrically insulated) of 3 mm diameter emitting 20 kHz sound with a power level set to 150 W cm^{-2} (calorimetrically determined). For electrochemical experiments a thermostatted cell,⁵ and a PAR 173 (EG&G) potentiostat controlled by an Oxford Electrodes programmer and connected to a Lloyd P3 plotter were used. Electrodes used were a 3 mm diameter glassy carbon disc (BAS), a graphite rod as a counter, and a saturated calomel reference electrode. Chemical reagents and electrolyte salt (Aldrich) were of highest commercially available quality.

‡ Bulk electrolysis experiments were performed typically with 200 mg substrate in a 20 ml electrolyte volume at a large surface area gold wire electrode and 150 W cm^{-2} ultrasound intensity.

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