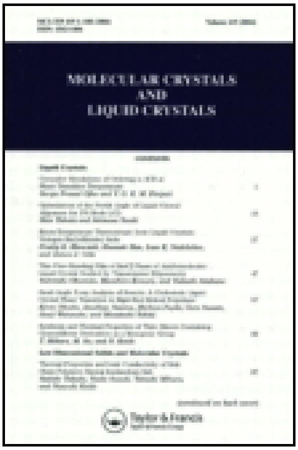

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Electrochemical Generation of Polymorphic Structures at Charged Aqueous Interfaces. An Example of Redox Couple Methylene Blue/ Leucomethylene Blue

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ELECTROCHEMICAL GENERATION OF POLYMORPHIC STRUCTURES AT CHARGED AQUEOUS INTERFACES. AN EXAMPLE OF REDOX COUPLE METHYLENE BLUE/LEUCOMETHYLENE BLUE.

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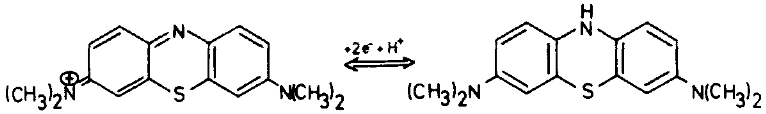
Abstract Leucomethylene blue (3,9-bis(dimethylamino)-phenathiazin) electrogenerated at the interface electrode/aqueous electrolyte solution forms several ordered structures which depend strongly on the potential and charge of the electrode surface and type of anions present at the interface. Interconversion between the structures, provoked by potential steps (1 mV - 1 V) is characterized by fast phase transitions corresponding to progressive two-dymensional nucleaiton and growth.

Kinetics and mechanism of the fast charge transfer process ($10^3 < k < 10^4$ s^{-1}) through the ordered multilayer films at mercury, gold and platinum electrodes are presented.

INTRODUCTION

Leucomethylene blue (3,9-bis(dimethylamino)phenathiazin electrogenerated at the interface electrode/aqueous electrolyte solution:



(1)

(MB) (LMB)

forms several ordered structures which depend strongly on the electrode surface and type of anions present at the interface[1]. Interconversion between the structures, provoked by potential steps (1 mV - 1 V) is characterized by fast phase transitions corresponding to progressive two-dimensional nucleation and growth[2].

METHODOLOGY

Electroactive organic molecules can be studied in the adsorbed state by modern electrochemical relaxation techniques[3].

Fast potentiostatic perturbation at the dropping mercury electrode (Fig. 1) is particularly suited for the study of phase transitions[4] (Fig. 2).

$$i = q_{mon}\,\pi\,k_N\,k_G^2\,t^2\,\exp\left(-\frac{\pi}{3}\,k_N\,k_G^2\,t^3\right) \qquad (2)$$

i is current, $\mathbf{q_{mon}}$ charge corresponding to the monolayer formation (or transformation), $\mathbf{k_N}$ is the rate of formation of the nuclei and $\mathbf{k_G}$ the growth rate.

Chronocoulometric results allow precise evaluation of surface concentrations (Γ_o):

$$Q = 2\,n\,F\,A\,D_o^{1/2}\,C_o^{*}\,t^{1/2}\,\pi^{1/2} + Q_{dl} + n\,F\,A\,\Gamma_o \qquad (3)$$

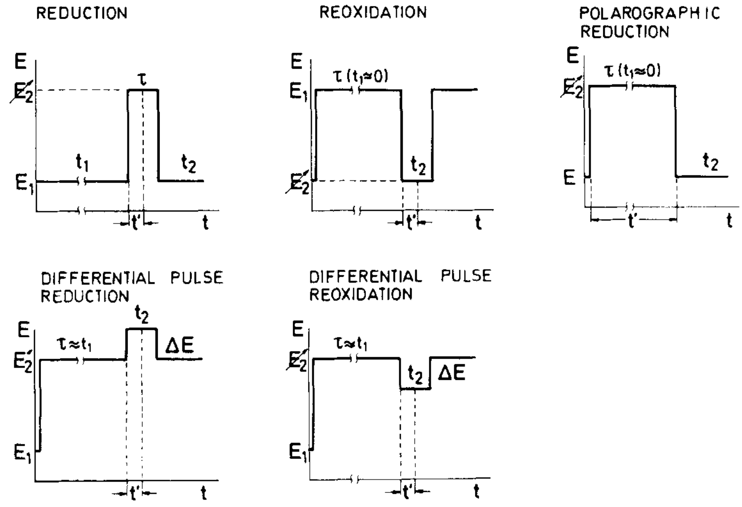


FIGURE 1. Programmed sequence of potentials in the potentiostatic relaxation experiments at the dropping mercury electrode; $\tau = 4$ s, t' is a typical time interval for measurement (integration) of the current response.

A - surface area of the electrode,

D_o - diffusion coefficient,

C_o^* - concentration in the solution,

n - number of electrons per molecule in oxidation or reduction,

Q_{dl} - charge devoted to double-layer capacitance.

and kinetics and mechanism of surface charge transfer reaction[5] (Fig. 3).

Cyclic voltammetry is used for qualitative characterization of surface structures at stationary electrodes (platinum, gold)[6,7].

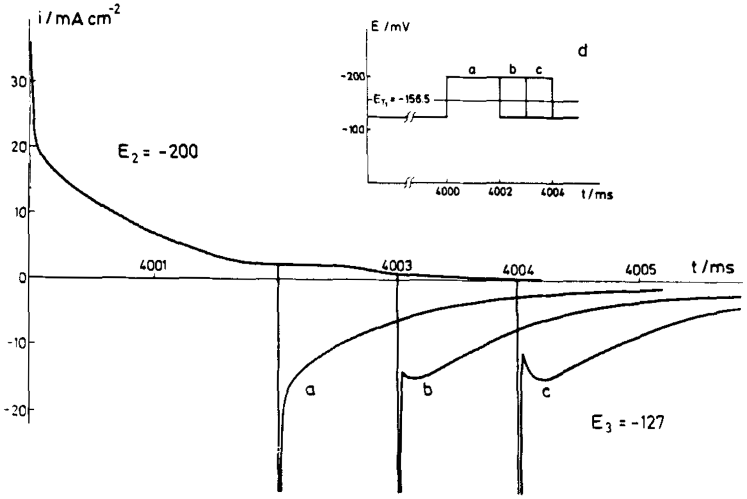


FIGURE 2. Current-time curves (at the dropping mercury electrode) with the maxima corresponding to the phase transition T_1 in the reduction of MB^+ and subsequent reoxidation of LMB. LMB generation is performed during 2 (a), 3 (b) and 4 (c) ms at $E_2 = -200$ mV ($E_2 < E_{T_1}$) and subsequent reoxidation is recorded at $E_3 =$ □ -127 mV ($E_3 > E_{T_1}$). The programmed sequence of potential steps (excitation signal) is indicated by the scheme (d).

RESULTS

MERCURY ELECTRODE

Mechanism of the charge transfer process and phase transitions in the adsorbed MB/LMB layers is schematically presented in Fig. 4. The phase transitions are fast (ms scale) and presence of nitrate ions is essential.

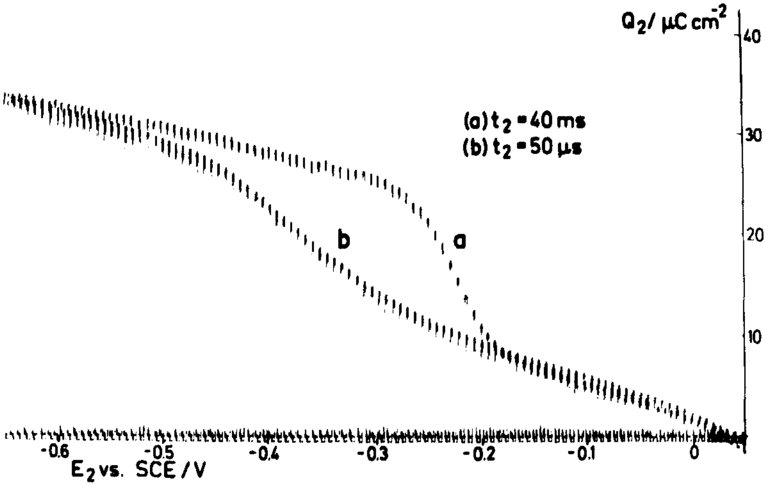


FIGURE 3. Reduction chronocoulograms at the dropping mercury electrode in 3×10^{-5} M MB, 1 M KNO_3 solution for the pulse duration (t_2): 20 µs and 40 ms. From the shift of the half-wave potential with the pulse duration (20 µs - 1 ms) kinetics and mechanism of the charge transfer are determined ($10^{-3} < k_o^a < 10^4\ s^{-1}$).

PLATINUM AND GOLD ELECTRODES

In presence of nitrate depending on the generation potential two different LMB phases were identified:

1. ordered phase with a very efficient charge transfer across a quasi-infinite (> 20) number of monolayers (distance between adjacent monolayers is 3 - 4 Å). Amplitude of the very narrow reoxidation wave is proportional to the generation time (Fig. 6);
2. less ordered phase with inefficient charge transfer:

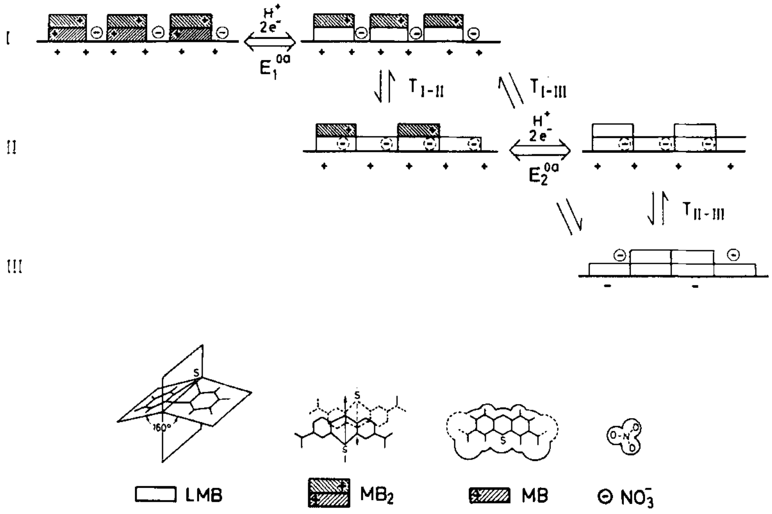


FIGURE 4. Mechanism of the charge transfer process and phase transitions (T_1 and T_2) in the adsorbed MB/LMB layer at the mercury electrode.

ill-defined and incomplete reoxidation, even at high overpotentials (200 mV).

The interconversion between two phases takes place in the time scale of seconds (Fig. 6b). Only at perfectly clean gold[6] and platinum[7] surfaces the ordered structure can be formed at the characteristic potential (-291 - -328 mV, identical for Pt and Au).

The structure is independent of the crystal planes of the electrode.

In fluoride solutions platinum and gold affect the electrogeneration of LMB differently:

1. at gold electrode several structures are formed with

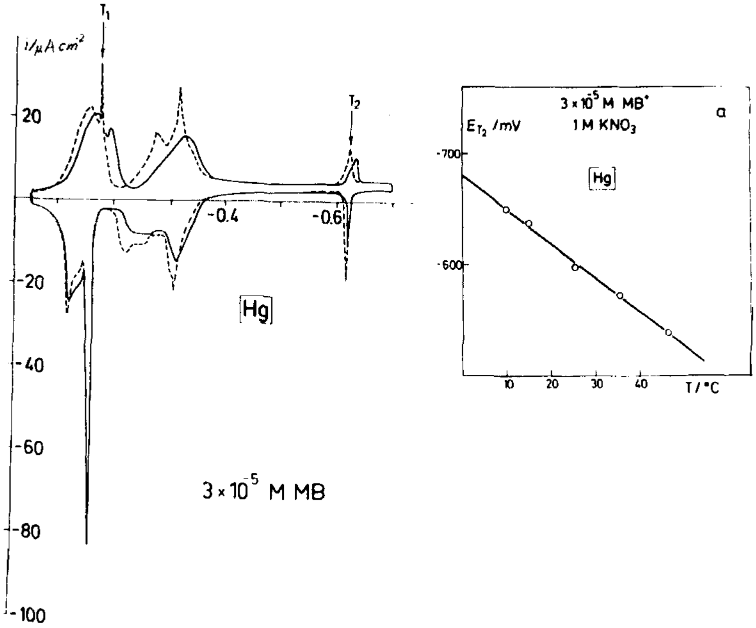


FIGURE 5. Cyclic voltammograms of MB/LMB in 3×10^{-5} M, 1 M KNO_3 solution at mercury drop electrode. Sweep rate = 50 mV/s, 25°C: first (——) and the second (---) subsequent cycle.
a) Effect of temperature on the potential of the second phase transition (E_{T_2}).

a complex dependence on the potential and time of generation (Fig. 7). The phase changes are significantly slower (minute time scale) than in nitrate ;

2. at platinum electrode predominantly one ordered phase is formed (Fig. 8).

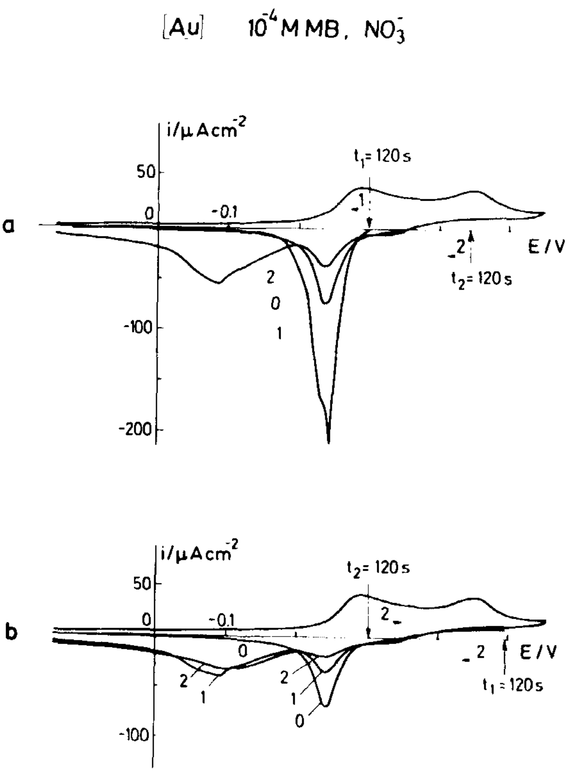


FIGURE 6. Effect of generation potential and time on LMB structure at the gold surface. Sweep rate □ 50 mV/s, $21^{\circ}C$, surface area of electrode: 11.6 mm².

a) curve 0: Cyclic voltammogram,
   curve 1: LMB reoxidation after 120 s reduction (generation) at E_1= -0.302 mV,
   curve 2: LMB reoxidation after 120 s reduction at E_2= -444 mV.

b) curve 0: Cyclic voltammogram,
   curve 1: LMB reoxidation after 120 s reduction at E_2 (same as curve a)2),
   curve 2: LMB reoxidation after subsequent reductions at E_1 (120 s) and E_2 (120 s). It shows that the structure formed at E_1 (reoxidation peak, curve a)1) is reorganized at E_2.

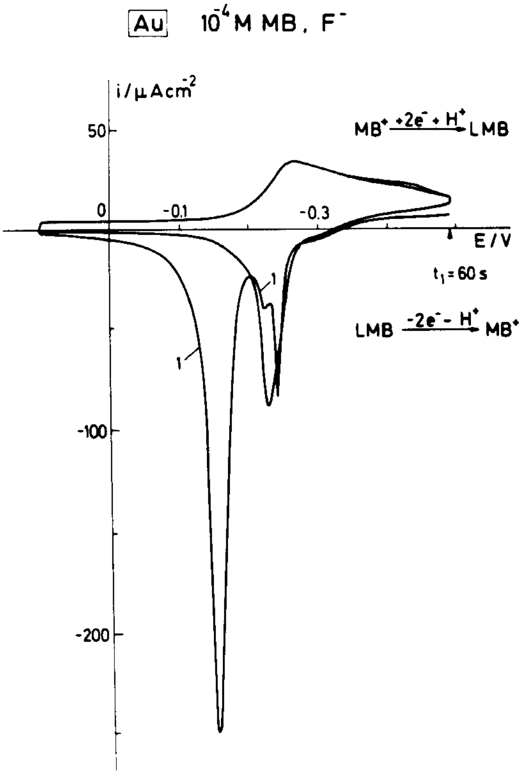


FIGURE 7. Cyclic voltammogram of MB/LMB at the gold electrode in 1 M fluoride solution. 60 s generation at -0.458 V results in formation of two distinct ordered structures (curve 1).
Sweep rate = 50 mV/s.

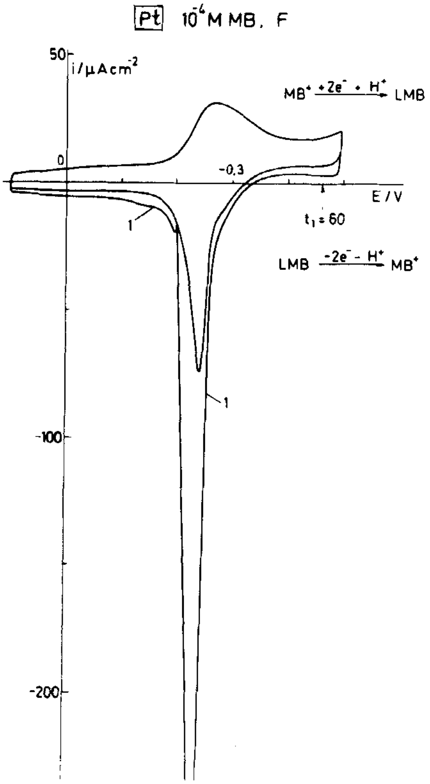


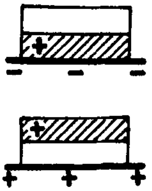
FIGURE 8. Cyclic voltammogram of MB/LMB in fluoride solution, platinum electrode. 60 s generation at -0.498 V results in one predominant ordered structure (curve 1).
Sweep rate = 50 mV/s, surface area of the electrode: 18.1 mm².

CHARACTERISTICS OF ELECTROGENERATED LMB STRUCTURES

1. Fast charge transfer through organized multilayers (infinite number of two-dimensional crystalline layers) in the adsorbed film at the electrode by redox self exchange[8,9] (hopping mechanism, $k_h \approx 10^4\ s^{-1}$).

2. Slower (Hg ≫ Pt > Au) process of reorganization of the adsorbed film due to lateral interactions between LMB molecules and dipole anion interaction.

3. Stabilization of the charge-transfer complex MB-LMB at the interface depends on the charge of the metal surface:



Pt, Au $E_{p.z.c.} \gg E^0_{MB/LMB}$

Hg $E_{p.z.c.} \ll E^0_{MB/LMB}$

4. Role of water of hydration: the effect of anions with different hydration (nitrate, fluoride) indicates the importance of water structure in the formation of ordered phases.

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