In-situ spectroelectrochemistry of adsorbed methylene blue on a sulphur-modified gold electrode

R.O. Lezna, N.R. de Tacconi, F. Hahn [*] and A.J. Arvia

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Sucursal 4, Casilla de Correo 16, La Plata (1900) (Argentina)

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Abstract

The properties of a methylene blue layer adsorbed onto a sulphur-modified gold electrode have been studied by electrochemical and in-situ reflectance spectroscopy in the visible region. At saturation coverage, methylene blue monomer and dimer bands were observed in the double-layer region through the electrochromism of the adsorbed film arising from the effect of the double-layer field on the molecule transition moment. Possible dye orientations in the adsorbed state are discussed with the aid of the optical measurements. At low surface concentrations, the optical signal stems from modulation of the monomer/dimer interconversion. Repeated electrochemical reduction and oxidation of adsorbed methylene blue result in gradual desorption of the dimer species, probably due to a change in the molecular geometry upon reduction which may evolve from a planar configuration to a folded structure.

INTRODUCTION

In recent years, the study of electrodeposited organic layers on electrodes has become a field of increasing interest owing to their potential application in, for instance, electrochromic devices, synthetic conducting materials, photogalvanic cells and electrocatalysis [1–4].

Methylene blue cation (MB^+) is known in connection with the determination of surface areas and cation exchange capacity of clays [5]. Its use as a model system in studies of the structural reorganization of water in dyes [6–8] and in photoexcitation processes in aqueous and biological systems is also well reported [9–12].

In conventional electrochemistry, there is ample literature dealing with the properties of the methylene blue redox transformation between its coloured and

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[*] Permanent address: Université de Poitiers, Laboratoire de Chimie 1, Electrochimie et Interactions, 40 Avenue du Recteur Pineau, 86022 Poitiers, France.

leuco states [13–15]. Recently the electrochemical behaviour of a methylene blue monolayer bound to a sulphur-covered gold electrode has been reported [16]. On the other hand, the adsorption of sulphur-containing compounds on noble metals, gold and silver, is a subject of current interest in our laboratory [17,18]. In this work, we deal with the optical properties of a monolayer of methylene blue adsorbed on a sulphur-covered gold electrode (enhanced chemisorption), in the absence of methylene blue in solution, with a view to obtaining information on the structure of the dye layer as well as on the mechanism of its reduction to the leuco state.

EXPERIMENTAL

The working electrode was a gold disc (Specpure, Johnson Matthey), encased in Kel-F, polished to a mirror finish with alumina and cleaned in an ultrasonic bath before being introduced in the deoxygenated supporting electrolyte. The electrolyte composition, 0.8 M NaF in 0.1 M sodium phosphate buffer of pH 7.9, was chosen as the most suitable in terms of stability of the bound MB^+. Solutions were prepared with redistilled Millipore water and p.a. grade reagents. Potentials were measured and are quoted against a saturated calomel electrode. The gold was cycled a few times between the onset of the hydrogen evolution reaction (HER) and the oxide formation (ca. a monolayer of oxide), until a clean, reproducible profile was obtained.

The electrode was then removed from the electrochemical cell and dipped successively in a 5×10^{-3} M Na_2S solution for 30 s and in an 8×10^{-6} M MB^+ solution for either 3 min or just a few seconds for the high and low MB^+ surface concentrations, respectively. Dye saturation coverages were obtained for adsorption times longer than 2 min as checked by cyclic voltammetry. The electrode was then returned to the electrochemical cell.

Optical measurements were taken with linearly p-polarized light at an incident angle of $60°$ using a specially designed visible reflectance spectrometer [19]. Measurements made on adsorbed methyl orange on a platinum electrode, used as a model system, reproduced the optical data reported in the literature [20]. Details of the experimental set-up, assembled in our laboratory for in-situ optical studies of electrochemical systems, have been described elsewhere [17]. Spectra recorded as a function of time were obtained with the aid of a computerized optical multichannel analyser (OMA) fitted with a cooled Si diode array capable of detecting changes of 1×10^{-5} in $\delta R/R$ with a time resolution (averaging time) of ca. 200 ms. Optical measurements with this machine were obtained with unpolarized light.

RESULTS AND DISCUSSION

The electrochemical behaviour of methylene blue adsorbed on a sulphur-modified gold electrode has been reported by Svetlicic et al. [16]. The voltammogram in Fig. 1, obtained in the absence of methylene blue in solution, shows two main potential regions, a zone of double-layer charging, between $+0.2$ and -0.2 V, and a
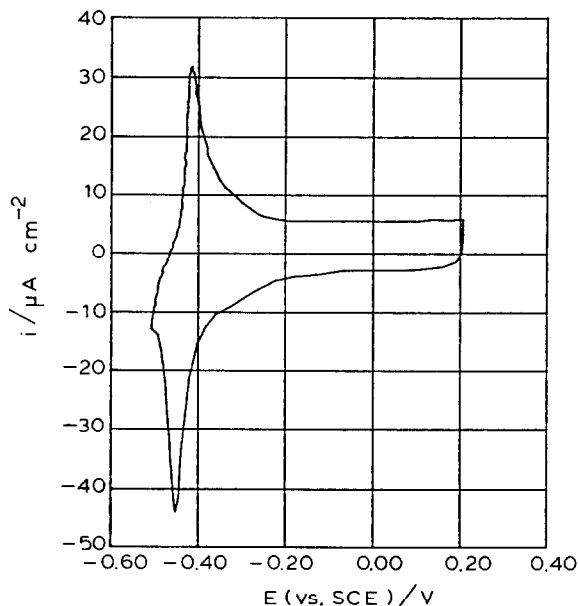
Fig. 1. Cyclic voltammogram of a methylene blue monolayer ($\Theta_{MB^+} \approx 1$) adsorbed on a sulphur-modified gold electrode in 0.8 M NaF with 0.05 M sodium phosphate buffer, pH 7.9. Initial potential = 0.2 V; $v = 50$ mV/s.

region characterized by a pair of sharp current peaks corresponding to the reversible MB^+/MBH reaction. This voltammetric profile does not undergo significant changes when cycled for a few times at 50 mV/s between $+0.2$ V and -0.5 V and involves a charge of 50 $\mu C/cm^2$ (saturation coverage) under the cathodic current peak and 45 $\mu C/cm^2$ for the anodic one.

It is worth noticing that the bound MB^+ species appears more stabilized on a sulphur-modified gold electrode than on bare gold, as confirmed by the negative potential shift of the MB^+/MBH electroreduction (postwave) in the presence of adsorbed sulphur [16].

Double layer region

High coverage
When the electrode potential is modulated at 11 Hz, with a 100 mV_{p-p} sinusoidal wave and bias potentials ranging from $+0.20$ to -0.15 V, two bands are detected at 1.79 and 2.05 eV, corresponding to the absorption of polarized radiation at the positive limit of the modulation by bound methylene blue monomer and dimer, respectively (Fig. 2). The intensity and shape of the bands were found to be independent of the bias potential and narrower than the absorption bands of the same species in solution (Fig. 2, inset) [21]. Absorption bands of solids are
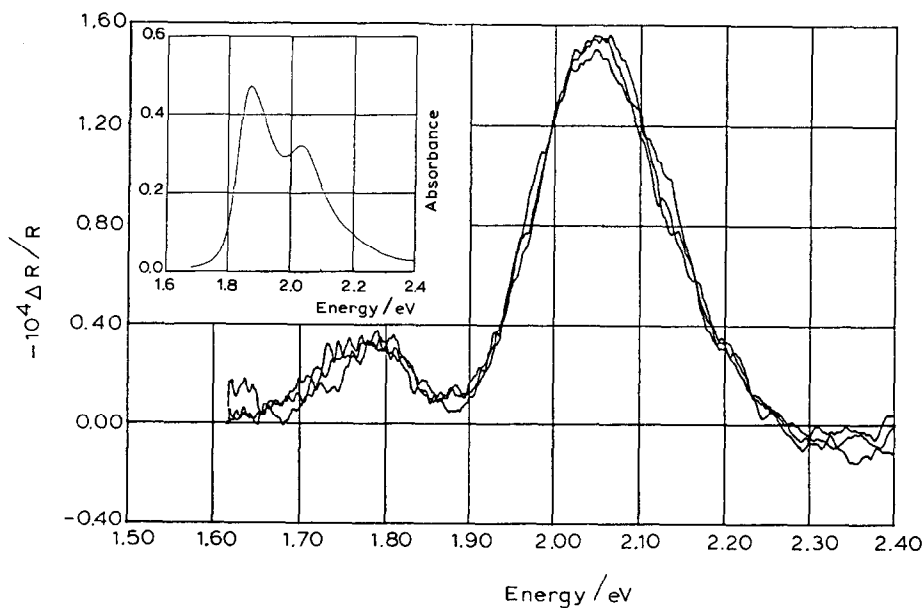
Fig. 2. Differential reflectance spectra of the $Au/S/MB^+$ film ($\Theta_{MB^+} \approx 1$) taken at 0.15, -0.05 and -0.15 V in the double-layer potential region. Supporting electrolyte: 0.8 M $NaF + 0.05$ M sodium phosphate buffer, pH 7.9. Angle of incidence, $\phi = 60°$; 100 mV_{p-p}; 11 Hz; p-polarization. Inset: spectrum of 8×10^{-6} M MB^+ in the supporting electrolyte.

frequently found to be narrower than their solution counterparts. However, this comparison should be made with caution as the mechanism of radiation absorption can be rather different in the two cases.

The intensity of the band assigned to the adsorbed monomer is lower than that of the bound dimer whereas the reverse intensity ratio is found in the solution from which the monolayer was adsorbed. In the 8×10^{-6} M MB^+ solution, monomers are the predominant species with the extent of aggregation of MB^+ being limited to dimerization [21]. Spectra obtained with unpolarized light (not shown) display a higher intensity for the monomer (relative to that of the dimer) than that found with p-polarized light, suggesting an unfavourable orientation for light absorption of the monomer species. The adsorbed monomer band is red-shifted by ca. 0.08 eV with respect to the corresponding value in solution. This result points to a strong interaction between the sulphur atoms of the modified surface and that of the MB^+ cation through the formation of a disulphide bond [16]. The shift to the red of the bound monomer band has also been reported for the adsorption of MB^+ on montmorillonite [22]. On the other hand, the dimer band shows practically no frequency change on adsorption. That is, according to the spectra observed in Fig. 2, the difference between the component bands at the two modulation limits, was found not to vary with the bias potential. These spectra may be interpreted by

assuming that the band intensities for both the dimer and the monomer increase linearly with the positive potential without undergoing changes in the frequency of the band maxima.

The optical response brought about by the potential modulation can be represented, neglecting contributions from the electroreflectance effect of the gold substrate, as follows:

$$\frac{1}{R}\frac{dR}{dE} = \frac{1}{R}\frac{\delta R}{\delta E}\bigg]_{\Theta} + \frac{1}{R}\frac{\delta R}{\delta \Theta}\bigg]_{E}\frac{d\Theta}{dE} \tag{1}$$

where the first term accounts for the effect of the double-layer field on the adsorbate absorption coefficient and represents electrochromism. The second term originates from the potential modulation of coverage.

The absence in the band shape of a derivative-like structure (Fig. 2), as would be expected for coverage modulation (monomer ↔ dimer transformation), and the potential region in which the bands are observed, the zone of double-layer charging, point to the electrochromism effect as the origin of the bands [23]. The static electric field in the double-layer is of the order of 10^7 V/cm; this high intensity is known to alter the absorption spectrum of adsorbed molecules on electrodes. There are two main contributions to the electrochromism of adsorbed species: the band shift and the change in the extinction coefficient due to the field dependence of the transition moment [24–26]. In solution, where restricted rotation of molecules is somewhat feasible there is a third contribution, the orientation effect, whereby the molecules reorient themselves to become aligned in an external field overcoming to a certain extent the temperature disorder. On the other hand, in an adsorbed layer the molecules hold rather fixed positions and therefore the orientational contribution can be excluded, at least in the functional form developed for molecules in solution.

In the present case, at saturation coverage, the position of the dimer and monomer bands shows no dependence on the bias potential. In addition, the band shapes for both species display no derivative-like structure (with respect to the photon energy). Consequently, the band shift effect seems to be absent in the optical response of the adsorbed methylene blue. According to the theory derived by Liptay [25] and Plieth et al. [26], the band shift effect can be expressed by equations as follows:

$$\text{ENERGY}_{F=F} = \left(|\mu_i| - |\mu_f|\right)\langle\cos\phi\rangle F + \text{ENERGY}_{F=F_0} \tag{2}$$

where μ_i and μ_f are the dipole moments of the ground state and the first excited state of the molecule, and ϕ is the angle between the dipole moments and the static field vector, F, which in turn is given by

$$F = F_0 + b\left(E - E_{F=F_0}\right) \tag{3}$$

F_0 being the field strength at the potential of zero charge (pzc) arising by oriented dipoles at the interphase. b is a proportionality constant termed the field strength factor, E is the potential and $E_{F=F_0}$ is the pzc.

Equations (2) and (3) would imply that either the difference between the dipole moments of the molecule in the ground and in the first excited state becomes practically zero or the angle between the double-layer electric field vector and the adsorbate dipole moments is 90°. Assuming that the dipole moment in the ground state lies in the molecular plane and that in the first excited state it is parallel to the one in the ground state, the perpendicularity between the static electric field and the dipole moments should indicate that the MB^+ molecules are adsorbed flat on the surface. This conclusion is at variance with other findings in this work and we will return to this point later.

The transition moment of a molecule in an external electric field may undergo changes due to the modifications of the wave functions of the final and initial states. A linear dependence of the wave function and the transition moment on the field strength is predicted by first-order perturbation theory. The analysis of this effect applied to the electrochemical interphase leads to relationships that depend linearly on either the modulation amplitude or both the modulation amplitude and the bias potential [26].

Methylene blue spectra in the double-layer region, i.e. at potentials more positive than that of the redox couple, were observed with both s- and p-polarized light, though with a higher intensity for polarization in the plane of incidence. According to FEMO (free-electron model) calculations, the transition moment in the methylene blue molecule lies in the ring plane [22]. As the transition moment, or its components, has to be aligned with both the oscillating electric vector of the light and the interphase electric field in order to give rise to absorption by the electrochromic effect, and, besides, absorption is detected for both polarizations, the methylene blue molecule should be oriented on the surface at a certain intermediate
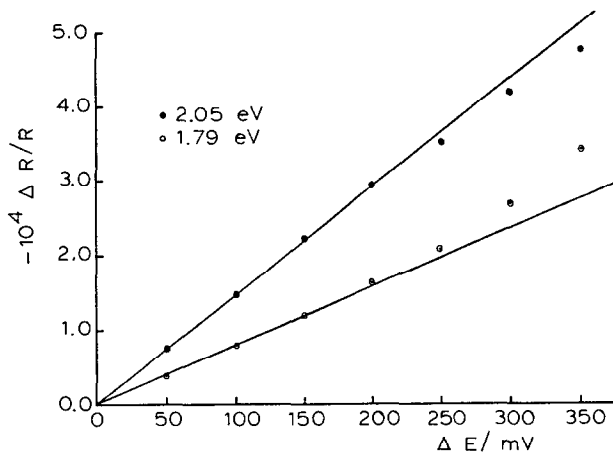

Fig. 3. Peak height for the bound methylene blue monomer (at 1.79 eV) and dimer (at 2.05 eV) as a function of the modulation amplitude (integral measurements). $\Theta_{MB^+} \approx 1$; $\phi = 60°$; 11 Hz; p-polarization.
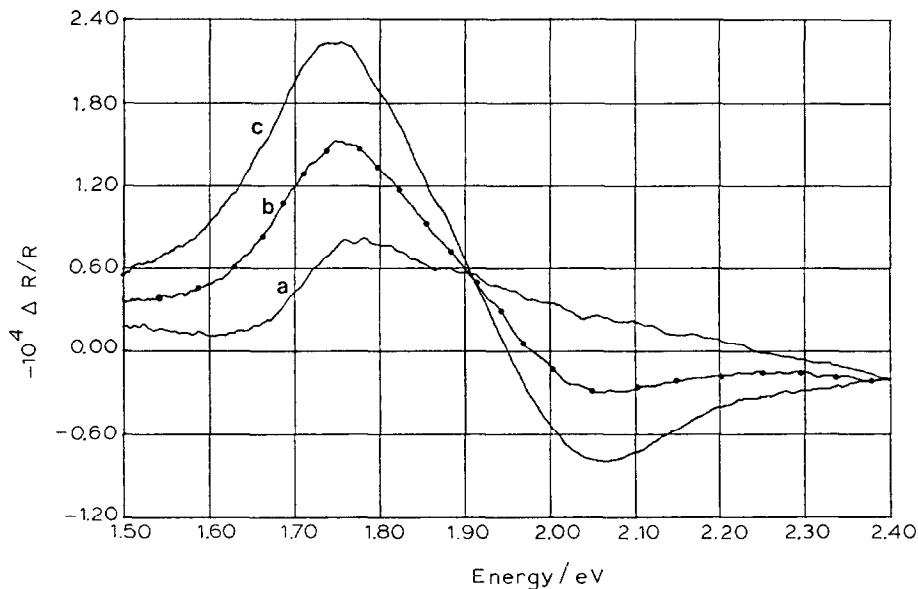
Fig. 4. Differential reflectance spectra of the Au/S/MB$^+$ layer ($\Theta_{MB^+} \approx 0.3$) taken with a modulation amplitude of 100 mV$_{p-p}$ centred at (a) 0.2 V, (b) 0.0 V and (c) -0.15 V. 0.8 M NaF $+0.05$ M sodium phosphate buffer, pH 7.9; $\phi = 60°$; 40 Hz; p-polarization.

angle to the surface normal. Moreover, the band intensities were found to be linearly dependent on the modulation amplitude (Fig. 3), a result to be expected if the optical response originates from the influence of the interfacial static electric field on the transition moment of the bound molecule. Deviation from linearity observed at high amplitudes should arise from modulation of the charge transfer process.

Low coverage

A quite distinct behaviour was found for methylene blue coverages lower than that of a monolayer (cathodic voltammetric charge 15 μC/cm^2). In this case, two bands of opposite signs were detected at the frequencies corresponding to the bound monomer (negative sign, absorption of light at the positive potential) and the bound dimer (positive sign, absorption of light at the negative end of the modulation) (Fig. 4). The band intensities increase with increasing negative bias potential and an isosbestic point can be observed, indicating the presence of two species on the surface. These bands should arise from the dimer/monomer interconversion brought about by the potential modulation, that is, the coverage term in eqn. (1) can be split into two contributions arising from the rate of coverage change with potential for monomer and dimer.

$$\frac{1}{R} \frac{\delta R}{\delta \Theta} \bigg]_E \frac{d\Theta}{dE} = k_{mon} \frac{d\Theta_{mon}}{dE} - \tfrac{1}{2} k_{dim} \frac{d\Theta_{dim}}{dE} \tag{4}$$
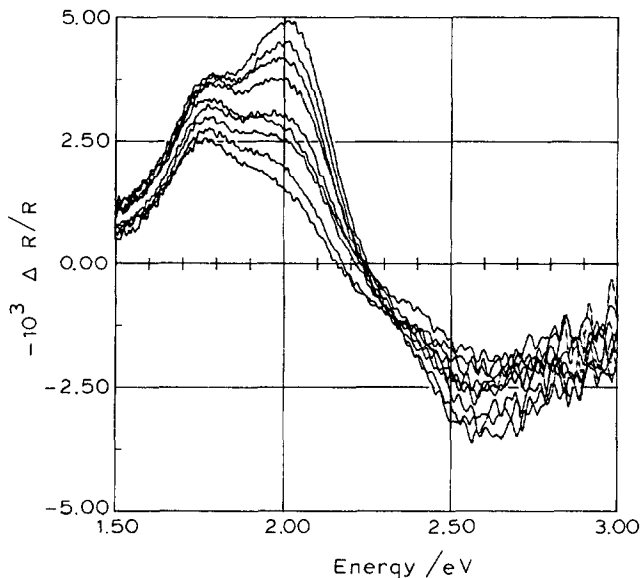
Fig. 5. Time dependence of the bound methylene blue couple modulation, integral measurements, $\delta R/R = (R_{\text{leuco}/-0.5\,\text{V}} - R_{\text{coloured}/-0.2\,\text{V}})/R_{\text{coloured}/-0.2\,\text{V}}$. Averaged spectra (ten repeats) were taken at 3 min intervals with an OMA system. Supporting electrolyte: 0.8 M NaF + 0.05 M sodium phosphate buffer, pH 7.9. $\phi = 60°$; modulation frequency: 8 Hz.

where k_{mon} and k_{dim} are wavelength-dependent coefficients for the monomer and dimer, respectively. The differential curve a in Fig. 4, taken at $+0.2$ V, displays only the monomer species, whereas for more negative potentials (curves b and c) both monomer and dimer species can be observed. This behaviour accounts for the minus sign of the dimer term in eq. (4), assuming the total coverage to be constant.

Coloured / leuco transition

At potentials more negative than -0.3 V, the adsorbed coloured form of methylene blue (cationic) undergoes an electroreduction process yielding the neutral (leuco) species MBH [27]:

$$MB^+ + e^- + H^+ \rightarrow MBH^{\cdot+}$$
$$MBH^{\cdot+} + e^- \rightarrow MBH \tag{5}$$

However, our findings suggest that this mechanism does not represent the system behaviour, at least in the adsorbed state, as it takes into account only the bound monomer and we have detected dimer species adsorbed throughout the double-layer region (Fig. 2), even at potentials just before the onset of the redox transformation.

Figure 5 shows a set of spectra obtained by subtracting the reflectance at -0.5 V (leuco) from that at -0.2 V (coloured) using a frequency of 8 Hz. Each spectrum (average of ten repeats at each potential) was taken at ca. 3 min intervals using an

OMA system. The waiting (initial) potential was held in the coloured region, as slow desorption was found to occur for sitting potentials in the bleached zone.

The spectra display two bands in the red region at 1.79 and 2.03 eV corresponding to bound monomer and dimer, respectively, absorbing radiation at the most positive potential (-0.3 V). The dimer band, which is more intense than the monomer band in the first series of spectra, gradually loses intensity to the monomer band and becomes a shoulder in the ninth spectrum. On the other hand, the monomer band increases its intensity in the first curve series, that is, a practically constant height is observed for this band although the baseline, blue tailing of the dimer band, is clearly decreasing.

The spectra measured in the potential region spanning the coloured/bleached switching presents a reproducible broad feature at ca. 2.67 eV which may arise from a species absorbing light at the negative potential limit, that is, with the methylene blue in the leuco (MBH) state. The origin of this structure in the spectra is not clear. However, the intermediate MBH˙, in its protonated form, has been reported as a light absorber at 2.95 eV in solution [28,29] and it may account for this band assuming a longer lifetime for this species in the adsorbed state than in solution.

In agreement with this supposition, the ac current profile (ac voltammetry, not shown) matches that of the differential optical response at 2.67 eV carried out under similar experimental conditions. Thus, the band seems to be related to the electrochemical reaction taking place in the adsorbed layer and not, for instance, to a change in the electroreflectance effect of gold arising from changes in the double-layer charge. No effect of the potential modulation on the underlying sulphur layer can give rise to this optical feature, as the same structure is found by modulating the couple of methylene blue adsorbed on gold without the sulphur coating.

The gradual disappearance of the dimer may be accounted for by the change in the molecule configuration on electroreduction. The initial MB$^+$ planar structure that favours the π-electron interaction between the rings, and therefore contributes to the dimer stability, evolves into a folding structure with the benzenic planes at a certain angle dictated chiefly by the change in hybridization of the nitrogen and sulphur hetero-atoms [30]. Thus, the nitrogen and sulphur atoms go from an sp^2, planar hybridization in the coloured form, to an sp^3, tetrahedral in the leuco species. As a result of this reorganization, a monomer may come off the structure and either go into the solution or become adsorbed itself. However, dimers were found in the spectra, though with less intensity or as a shoulder, even after long modulation times (e.g. 15 min), particularly when the modulation frequency was relatively high, ca. 11 Hz. This result appears to be consistent with either the presence of distorted dimers, probably with short lifetimes, in the leuco state or a relatively fast recombination of MB$^+$ monomers to give dimers at the more positive potential. The latter process should proceed through steric reorganizations, not necessarily simple considering that we are dealing with bound species without counterparts in solution.

After repeatedly pulsing the electrode, the whole spectral profile in the red region is attenuated, that is, the bound monomer is also partially desorbed in the leuco state. The electrodesorption of neutral molecules at sufficiently negative potentials

is a well-known result in adsorption studies [31]. Moreover, the deposition of a monolayer of sulphur on gold shifts the pzc towards more positive potentials. Therefore, the bound monomer sees a more negative surface than it would on a bare gold electrode.

CONCLUSIONS

Properties in the adsorbed state of a methylene blue layer have been investigated by electrochemical and in-situ reflectance methods.

For a monolayer of methylene blue, two species, namely, dimers and monomers, were observed through their absorption bands as the potential was modulated in the double-layer region. The monomer band was found to be red-shifted by 0.08 eV (30 nm) with respect to that of the corresponding species in solution. This behaviour is associated with the formation of a disulphide bond between the dye sulphur atom and that of the coating layer. The bound dimer band appeared unshifted. Both bands are originated in the electrochromic effect. The absence of derivative-like spectra and the dependence of the band intensity on the light polarization and the modulation amplitude indicate that the electrochromism arises from the effect of the double-layer field on the molecule transition moment. Dye molecules seem to be adsorbed, on average, at an intermediate angle to the surface normal.

At low coverage, the relative amount of monomers and dimers was found to be a function of the bias potential, the relative amount of dimers increasing with the negative potential. The optical signal in this case stems from modulation of coverage.

At the onset of the electroreduction, dimers are the predominant species. As the MB^+ electroreduction is attended by a change in structure from a planar configuration (favourable towards dimerization) to a folded one, repeated transformations between leuco and coloured states (as those taking place during potential modulation) lead to a gradual disappearance of bound dimers. Both species, dimers and monomers, become desorbed for long modulation times.

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