

# Two-dimensional condensation of nucleic acid components at mercury film and gold electrodes

Stanislav Hasoň<sup>a,b</sup>, Vladimír Vetterl<sup>a,b,\*</sup>

<sup>a</sup>Department of Physical Electronics, Laboratory of Biophysics, Faculty of Science, Masaryk University, Kotlářská 2, CZ-611 37 Brno, Czech Republic

<sup>b</sup>Institute of Biophysics, Academy of Science of the Czech Republic, Královopolská 135, CZ-612 65 Brno, Czech Republic

Received 26 June 2001; received in revised form 7 September 2001; accepted 11 September 2001

## Abstract

The adsorption of cytidine at the mercury film electrodes and at the Au (111) single crystal electrode has been investigated. Some kinetic aspects such as the influence of pH and temperature on the formation or dissolution of cytidine adlayer on the pyrolytic graphite electrode covered by a mercury film or on the Au (111) have been studied. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Pyrolytic graphite electrode; Mercury film electrodes; Gold single crystal; Adsorption; Cytidine adlayers; Two-dimensional phase transition

## 1. Introduction

It is generally known that the nucleic acid bases and nucleosides form highly ordered two-dimensional (2D) adlayers in a broad range of pH and ionic strength at the mercury|solution interface [1–3].

The use of the mercury film electrodes (MFE) and/or solid electrodes has opened a new experimental field for the study of phase transitions and formation of condensed monolayer at the electrochemical interface [4]. Adsorption of the nucleic acid bases and nucleosides on Au (111) has been studied by several authors during the last 5 years [5–7]. The potential window for most of the solid electrodes is about 1 V more positive than for the MFE. The MFE are appropriate tools for the detection of the 2D condensation of nucleic acid bases and nucleosides at the potential window from –2.0 V to 0 V. Thus, we can investigate the effect of the structure of the substrate of solid electrode on the formation or dissolution of well-organized monolayers in the potential window used with a classical hanging mercury drop electrode (HMDE).

The aim of this work is the study of the kinetic aspects of phase transitions of the cytidine at the carbon electrode

covered by a thin mercury film and at the gold single crystal electrode Au (111).

## 2. Experimental

The electrochemical set-up consisted of a classical three-electrode system. The working electrode were: (A) a pyrolytic graphite electrode (PGE) covered by a thin mercury film and (B) a single crystal Au (111). The PGE was immersed into 0.2 M Hg(NO<sub>3</sub>)<sub>2</sub> water solution and treated at potential –1.0 V for 3 min. The area of the PGE covered by a mercury film was 0.205 cm<sup>2</sup>. The gold single crystal electrode Au (111) of diameter 4 mm was prepared according to a technique described by Hamelin [8]. The activation of the gold electrode Au (111) was described in detail in Ref. [9]. The counter electrode was a platinum wire. The reference electrode was: (A) Ag|AgCl|3 M KCl or (B) Hg|Hg<sub>2</sub>Cl<sub>2</sub>|KCl(sat).

The measurements were performed in a solution of 0.5 M NaCl (Merck, p.a.) with Britton–Robinson (BR) buffer or in 0.1 M KClO<sub>4</sub> (Fluka puriss., p.a.) with various additions of cytidine (Sigma).

The current measurements (*j*–*E*, *j*–*t*) and capacitance measurements (*C*–*E*) were performed using an electrochemical system AUTOLAB (Ecochemie, Utrecht, Netherlands) equipped with a potentiostat/galvanostat PGStat20 and a frequency-response analyser (FRA) module.

\* Corresponding author. Institute of Biophysics, Academy of Science of the Czech Republic, Královopolská 135, CZ-612 65 Brno, Czech Republic. Tel.: +42-5-41517143; fax: +42-5-41211293.

E-mail address: vetterl@ibp.cz (V. Vetterl).

### 3. Results and discussion

#### 3.1. Adsorption of cytidine at the MFE and single crystal electrode Au (111)

Fig. 1A shows the adsorption of 30 mM cytidine in 0.5 M NaCl+BR buffer in acid (pH 5.0) and alkaline solution (pH 8.3) at the PGE covered by a mercury film. In the acid solution cytidine forms only one physisorbed 2D condensed adlayer around  $-0.8$  V (region II). In the alkaline solution cytidine forms two different physisorbed 2D adlayers; the more negative adlayer around  $-0.8$  V (region II) and the other one around  $-0.1$  V (region III). Regions Ia and Ib correspond to the dilute and reversible physical adsorption of individual cytidine molecules (Fig. 1A). Similar adsorption behaviour of cytidine at the HMDE was described earlier by Temerk [10,11] and Ibrahim [12].

Fig. 1B,C shows that 50 mM cytidine in the acid (pH 4.2) and neutral solution (pH 7.0) forms at the Au (111) the physisorbed 2D condensed adlayer in potential window from  $-0.3$  V to  $+0.07$  V (region II). At positive potential (around potential  $+0.23$  V) cytidine forms ordered chemisorbed adlayer in acid and neutral solution (region IV). In contrast to region II, the extent of region IV is only slightly affected by temperature or concentration change (not

shown). These data confirm that the formation of layer II is caused by physical forces and in region IV cytidine is chemisorbed [13].

#### 3.2. Kinetics of transformations

The kinetics of the 2D condensation or dissolution has been studied by recording the current transients. We used the double potential step techniques [14]. The rate of the transients is characterised by the time  $t_{\max}$  at which the current reaches maximum.

We have studied the kinetics associated with the interfacial transformation of cytidine starting from the dilute adsorption region (Ia) to the physisorbed film (region II) at the MFE. The kinetics of dissolution of the chemisorbed layer of cytidine at the Au (111) was studied as well.

The current transients corresponding to the formation of the ordered physisorbed layer (region II) from dilute adsorption state Ia recorded for 30 mM cytidine in 0.5 M NaCl + BR buffer at pH 5.0 on the PGE covered by a mercury film at various temperatures show that the overall transformation becomes faster when the temperature is decreased (Fig. 1D). Such a result is expected for a condensation process since the activation energy is related to the formation of the critical nucleus and consequently to the supersaturation of the system

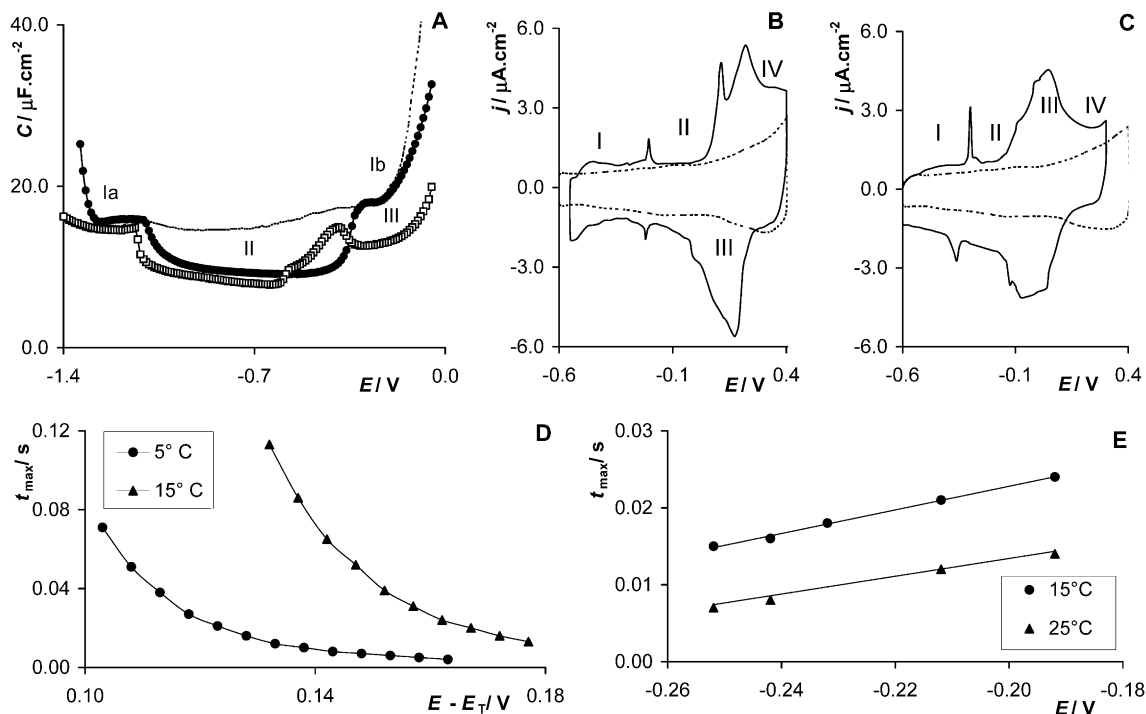


Fig. 1. (A) Capacitance–potential curves of 30 mM cytidine in 0.5 M NaCl with BR buffer at 10 °C on PGE covered by a mercury film at different pHs: (●) pH 5.0 and (□) pH 8.3. Potential was scanned from positive to negative values. The different adsorption states are labelled Ia, Ib, II and III. Dashed line represents the  $C$ – $E$  curve of the background electrolyte. (B) Current–potential curves of 50 mM cytidine in 0.1 M KClO<sub>4</sub> at pH 4.2 and (C) at pH 7.0 on Au (111). The different adsorption states are labelled I, II, III and IV. Dashed line represents the  $j$ – $E$  curve of the background electrolyte. The scan rate was 20 mV s<sup>−1</sup>. (D) Influence of the temperature on the rate of transformation Ia → II for 30 mM cytidine in 0.5 M NaCl + BR buffer at pH 5.0 on PGE covered by a mercury film. Transitions triggered by a potential step from  $-1.2$  V to various final potentials  $E$ ;  $E_T$  is the transition potential Ia → II. (E) Influence of the temperature on the rate of transformation IV → II for 50 mM cytidine in 0.1 M KClO<sub>4</sub> at pH 7.0 on Au (111). Transitions triggered by a potential step from  $+0.18$  V to various final potentials.

[15]. The effect of the temperature on the transition kinetics is more pronounced especially for low overpotentials; i.e. when the final potential  $E_f$  of the current transient is located close to the negative edge of the pit (region II). From Fig. 1D, it can be seen that at higher overpotentials the rate of transformation Ia  $\rightarrow$  II is less affected by the temperature. The observed influence of the temperature on the rate of transformation of film is typical for a non-faradaic condensation process controlled by a nucleation and growth mechanism.

The kinetics of dissolution of the chemisorbed layer of 50 mM cytidine in 0.1 M KClO<sub>4</sub> at pH 7.0 was studied at the Au (111). The overall rate of transformation of film IV into film II becomes faster when the temperature is raised (Fig. 1E) contrary to the effect of temperature on the rate of formation of the condensed physisorbed film II of cytidine at the PGE covered by a mercury film. The rate of transients IV  $\rightarrow$  II depends linearly on the final potential  $E$ .

#### 4. Conclusion

The adsorption and 2D condensation of cytidine at the MFE is very similar to that observed at the HMDE. Cytidine forms at the Au (111) distinct films ranging from a dilute adsorbed state to a condensed physisorbed film and an organized chemisorbed layer. The temperature dependence of the rate of transformation provides clear evidence about the nature of the interfacial processes of cytidine at the different substrates.

#### Acknowledgements

This work was supported by Grant Agency of the Ministry of Education, Youth and Physical Training of the Czech Republic "Fund for Development of Universities" G4 0583 (S.H.), Grant Agency of the Academy of Sciences of the Czech Republic A4004002 (V.V.).

The authors wish to thank Prof. C. Buess-Herman for her help and valuable discussion during the stay of one of us (S.H.) in her laboratory (Université Libre de Bruxelles).

#### References

- [1] V. Vetterl, Alternating current polarography of nucleotides, *J. Electroanal. Chem.* 19 (1968) 169–173.
- [2] C. Buess-Herman, Phase transitions in adsorbed layers, in: A.F. Silva (Ed.), *Trends in Interfacial Electrochemistry and Electrochemical Engineering*, NATO ASI Ser., Reidel Publishing, Dordrecht, 1986, pp. 205–253.
- [3] R. de Levie, The dynamic double layer: two-dimensional condensation at the mercury–water interface, *Chem. Rev.* 88 (1988) 599–609.
- [4] C. Buess-Herman, Dynamics of adsorption and two-dimensional phase transitions at electrode surfaces, in: J. Lipkowski, P.N. Ross (Eds.), *Adsorption of Molecules at Metal Electrodes*, VCH Publishers, New York, 1992, pp. 77–118.
- [5] C. Buess-Herman, Self-assembled monolayers at electrode metal surfaces, *Prog. Surf. Sci.* 46 (1994) 335–375.
- [6] M. Van Krieken, C. Buess-Herman, On the dissolution kinetics of two-dimensional uridine layers adsorbed on gold single-crystal electrodes, *Electrochim. Acta* 43 (1998) 2831–2841.
- [7] T. Wandlowski, D. Lampner, S.M. Lindsay, Structure and stability of cytosine adlayers on Au(111): an in-situ STM study, *J. Electroanal. Chem.* 404 (1996) 215–226.
- [8] A. Hamelin, Double-layer properties at sp and sd metal single-crystal electrodes, in: B.E. Conway, R.E. White, J.O.M. Bockris (Eds.), *Mod. Aspects Electrochem.*, vol. 16, Plenum, New York, 1985, pp. 1–101.
- [9] J. Clavilier, R. Faure, G. Guinet, R. Durand, Preparation of monocrystalline Pt microelectrodes and electrochemical study of the plane surfaces cut in the direction of the (111) and (110) planes, *J. Electroanal. Chem.* 107 (1980) 205–209.
- [10] Y.M. Temerk, P. Valenta, Electrochemical behaviour of mono- and oligonucleotides: Part V. Voltammetric studies on the adsorption stages and interfacial orientations of cytidine at charged interfaces, *J. Electroanal. Chem.* 93 (1978) 57–67.
- [11] Y.M. Temerk, Studies on the adsorption and the association of cytidine sulphate at the dropping mercury electrode with phase-sensitive apolarography, *Can. J. Chem.* 57 (1979) 1136–1140.
- [12] M.S. Ibrahim, Adsorption stages and interfacial orientations of cytidine sulfate at the mercury/electrolyte interface, *Electrochim. Acta* 40 (1995) 1913–1919.
- [13] M.H. Hözlze, D.M. Kolb, D. Krznaric, B. Cosovic, Adsorption and phase formation of uracil derivatives on gold and silver single-crystal electrodes, *Ber. Bunsen-Ges. Phys. Chem.* 100 (1996) 1779–1790.
- [14] C. Buess-Herman, Non-faradaic phase transitions in adsorbed organic layers: Part 2. Experimental aspects, *J. Electroanal. Chem.* 186 (1985) 41–50.
- [15] C. Buess-Herman, S. Bare, M. Poelman, M. Van Krieken, Ordered organic adlayers at electrode surfaces, in: A. Wieckowski (Ed.), *Interfacial Electrochemistry: Theory, Experiment and Applications*, Marcel Dekker, New York, 1999, pp. 427–447.