

# Discovery of two-dimensional condensation of nucleic acids components at the mercury electrodes – 45 years' history

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## Abstract

Purine and pyrimidine derivatives currently occurring in nucleic acids possess an extraordinary high ability of self-association at the electrode surface and can form there by a two-dimensional (2D) condensation a compact self-assembled monolayer. By this high condensation ability nucleic acid bases differ from most of the other purine and pyrimidine derivatives which currently do not occur in nucleic acids. A regular arrangement of nucleic acid bases, nucleosides and nucleotides leading to 2D condensation takes place not only at the liquid mercury surface, but also on the mercury film modified carbon/graphite, solid amalgam, or atomically flat single-crystal metal electrodes. With polymeric DNA and/or polynucleotides this kind of 2D condensation has not been observed. Recently, we have shown that synthetic homo- and hetero-pyrimidinic oligodeoxynucleotides (ODNs) can 2D condensate at the negatively charged mercury and solid amalgam surfaces. Formation of the ODN condensed film took place even in the absence of any ODN in the bulk solution (*ex situ* 2D condensation). No such 2D condensed monolayer was observed with homo- and hetero-purinic ODNs giving only tensammetric (desorption/reorientation) peaks in weakly alkaline pHs within the same potential region.

**Keywords:** Two-dimensional condensation, adsorption, mercury-based electrodes, adenosine, cytidine, oligodeoxynucleotides

## Introduction

The adsorption of nucleic acids at the electrodes can be followed by measurement of the impedance and/or differential capacitance of the electrode double layer, as it was done for the first time in 1961 by Miller (Miller, 1961). In 1965 one of us (VV) discovered that nucleic acid bases as well as some of the nucleosides and nucleotides currently occurring in nucleic acids possess an

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extraordinary high ability of self-association at the electrode surface and can form there by a two-dimensional (2D) condensation a monomolecular compact film (Vetterl 1965; Vetterl 1966).

## Discussion

The driving forces leading to 2D condensation of nucleic acid bases are hydrogen bonds between flat oriented adsorbed molecules and/or stacking interactions between perpendicularly oriented molecules to the electrode surface. In the presence of the 2D condensed films all solvent molecules are replaced from the electrode surface by the condensed nucleic acids components and thus the differential capacitance of the electrode double layer is depressed considerably, giving rise to a characteristic “pit” on capacitance-potential (*C-E*) curves and sharp spikes on cyclic voltammograms (CVs). The positions of both current spikes and pit edges strongly depend on the direction of the potential scan (hysteresis) as shown in Fig 1, and the width of this condensed film decreases with increasing temperature. These characteristics are

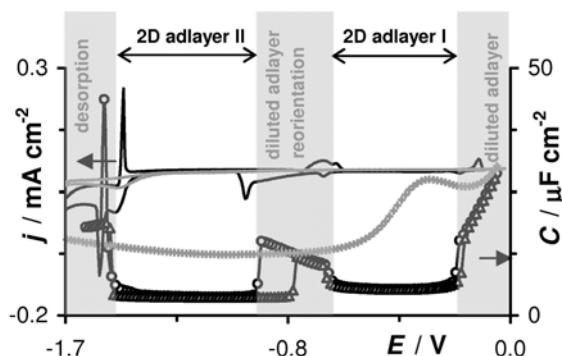


Figure 1: Cyclic voltammogram and capacitance-potential (*C-E*) curves of 14 mM adenosine at pH 5 in 0.1 M NaCl on the hanging mercury drop electrode (HMDE). Potential scan from -0.05 V to negative values (○) and in the opposite direction (Δ). Gray line and (+) represent the CV and *C-E* responses of background electrolyte, respectively. All measurements were performed at 5° C with scan rate 1 V s<sup>-1</sup> (CV) and frequency 33 Hz, *ac* voltage amplitude 5 mV, integration time 2 s (*C-E* curves).

typical properties of 2D physisorbed condensed films (Buess-Herman 1994). From a quadratic dependence of the capacitance pit

width on temperature and/or from a surface tension measurement was possible to determine the interaction energies of adsorbed molecules and calculate the area occupied per one adsorbed molecule, which gave information about orientation of molecules at the electrode surface (Brabec et al. 1996). With the monomeric nucleic acid bases, the capacitance pits (2D adlayer I in Fig 1) on the mercury electrode were observed usually (with the exemption of cytosine) at potentials close to the potential of zero charge (at about -0.5 V). In contrast, some of the purine and pyrimidine nucleosides formed at the negatively charged surface a second 2D condensed film (2D adlayer II in Fig 1) in which the adsorbed molecules have a different orientation (Hason et al 2002a).

The formation of 2D condensed films on homogenous surface is characterized by the presence of phase transitions. The kinetics of the film formation can be studied by potential jump experiments and often proceed via nucleation and growth processes. Depending on the start and final potentials different shapes of capacitance or current transitions can be detected. The transitions can be analyzed by Avrami theorem (Buess-Herman 1994).

At the beginning of the 1990s, it was observed that the nucleic acid components can form 2D condensed films also on basal faces of single crystal electrodes (Wandlowski 2002). Recently, we have shown that solid amalgam electrodes (thickness of amalgam layer was 40 nm) can be successfully used as a cheaper alternative to very expensive single-crystal metal electrodes for the study of the adsorption, formation of 2D condensed film (for more details see Fig 2) and kinetics of the phase transitions of nucleic acids components (Hason et al. 2004a,b) and adsorption behavior of synthetic ODNs (Hason et al. 2008). 2D condensation can be also studied on the carbon/graphite electrodes modified with a mercury films whose thicknesses are higher than 200 nm (see curve (e) in the Fig 2). In the case of thin (several tens of nanometers) mercury film electrodes was observed that Hg exists on the carbon surfaces in the form of inhomogeneously scattered droplet of different diameter (Hason et al. 2002b,c; Hason et al. 2003) and thus these electrodes have a small sensitivity to detection of the 2D condensation adlayers. In addition, these mercury film electrodes have a low lifetime in comparison with solid nontoxic amalgam electrodes.

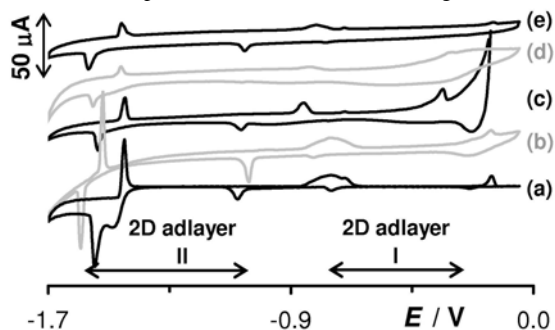


Figure 2: CV curves of 14 mM adenosine at pH 5 in 0.1 M NaCl on the: (a) HMDE, (b) PtAE, (c) CuAE, (d) AgAE, and (e) Hg-PGEb. Two different 2D physisorbed condensed adlayers of adenosine in the acid pH, first of these exists at about -0.5 V, and the second is centered at potential of -1.2 V, are for all mercury hanging drop, solid amalgams, and pyrolytic graphite electrode modified by a mercury film delimited by the sharp current peaks. All measurements were performed at 5° C with scan rate 1 V s<sup>-1</sup>. The thicknesses of the amalgam layers deposited on the metal substrates and mercury film on the cleaved pyrolytic graphite in basal orientation were 40 nm and 200 nm, respectively.

## Conclusion

We have shown that solid amalgam electrodes can serve as an effective tool for study of the adsorption, formation of 2D condensed films and kinetics of the phase transitions of nucleic acids components. We also for the first time demonstrated that synthetic homo- and hetero-pyrimidinic ODNs can 2D condensate at the negatively charged solid amalgam electrodes. Homo- and hetero-purinic ODNs did not form these 2D physisorbed condensed monolayers, only produce tensammetric (desorption/reorientation) peaks in weakly alkaline pHs within the same potential region.

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