

THE ELECTROCHEMICAL PROPERTIES OF THE PURINE BASES: AT THE INTERFACE BETWEEN BIOLOGICAL CONJUGATES TO INORGANIC SURFACES

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Introduction

The study of the charge transfer and interfacial reactions of the purine bases in physiological solutions provides valuable knowledge, as these processes are relevant to the origins of life.¹ It has been proposed that the adsorption of the purine bases on an inorganic surface could serve as a template for specifying the arrangement of amino acids in peptides. This in turn, would mimic the role of the bases in RNA; adenine is one of the constituent bases in ribonucleic acid (RNA) and deoxyribonucleic acid (DNA). Independent scanning tunneling microscopy experiments on Au(111) and graphite substrates show that adenine spontaneously self-assembles onto the surface.^{2, 3} The condensate morphology is method-dependent. Using 0.1 M NaCl as a supporting electrolyte, Srinivasan *et al* condensed adenine layers onto graphite, often with a multi-domain structure. Using the strong acid NaClO₄ as a supporting electrolyte, Tao *et al* observed that adenine condenses on Au(111) substrates by forming polymeric aggregates stacked with a periodicity of 3.4 ± 0.2 Å. Thus, for an inorganic surface, the aperiodic arrays or polymeric accretions formed on crystalline surfaces by adsorbed bases might still enable their participation in a primitive coding process. In this process, the interfacial charge transport and redox properties between the adsorbed and solution species are critical. In this presentation, preliminary results are given for the electrochemical behavior of the purine base, adenine (6-aminopurine), in physiological solutions (NaCl) using cyclic voltammetry on a gold working electrode.

Experimental

The electrochemical measurements were conducted in a standard three-electrode cell. A platinum (Pt, $\phi = 0.5$ mm) wire was used as the counter-electrode. The potentials are reported against an Ag/AgCl/KCl (3M) reference electrode. A gold wire (Au, $\phi = 0.5$ mm) was employed as the working electrode. The electrolytes employed are physiological: 1) a blank solution, H₂O + 0.1 M NaCl, and 2) H₂O + 0.1 M NaCl + 0.1mM adenine. Purified de-ionized (DI) water was employed. The NaCl and adenine were

high-purity crystals from Sigma. The electrolytes were de-aerated by bubbling high-purity nitrogen through the cell for at least 12 hours prior to all measurements. The bubbling rate was reduced during measurements. All data reported were reproducible; shown are representative single-examples of measurements conducted in identically prepared solutions. Prior to each measurement series, the Au and Pt electrodes were polished under water using metallographic methods, and given a final polish with a polymer-backed 0.3 μ m Al₂O₃ paper. The still wet working- and counter-electrodes were then ultrasonically cleaned (DI-H₂O) and transferred immediately into the electrochemical cell. Multiple cyclic voltammograms (CVs) were conducted with a Princeton Applied Research model 273A potentiostat, with scan rates ranging from 0.10 to 20 mV/sec. All CVs presented were started from the equilibrium open-circuit cell potential V_{oc} .

Results

The molecular structure of adenine is shown in Fig.-1. The hydrogen atoms (●) on the amino group (N₆) bonded to C6 of the purine ring, and the N9 nitrogen are proton donors, while the ring nitrogens N1, N3, and N7 are proton acceptors.

A representative CV (1mV/s scan rate) conducted in the blank 0.1 M NaCl solution is shown in Fig.-2. The forward scan (+V) CV data show a minimal interfacial capacitance, and no anodic or cathodic current waves on scanning between -1.0 to 1.1 V vs. Ag/AgCl. For a solution containing 0.1 mM adenine,

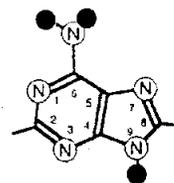


Fig. - 1: Adenine molecule.

CVs conducted in the forward direction (+V) exhibit a CV similar to that of Fig.-2. CVs started in a negative direction (1mV/s scan rate) exhibit a strong reduction peak, with $V_{peak} \approx -0.2$ V (see Fig.-3). On the forward scan, a weak, broad anodic current wave is observed starting at ≈ 0.4 V. Upon cycling back

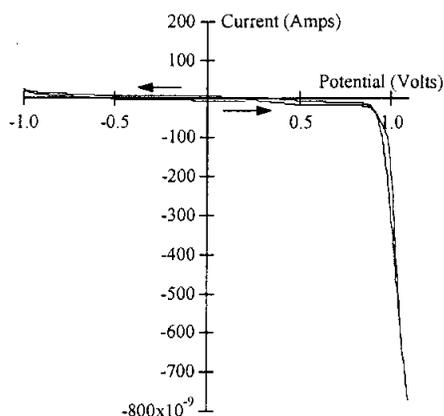


Fig.-2: CV in NaCl electrolyte. Scan rate: 1mV/s.

from the positive vertex potential, a current wave with reduced amplitude and two discernible peaks ($\Delta V_p = 127$ mV, $I_{p1}/I_{p2} = 0.87$) are revealed. CVs conducted at a scan rate of 0.10 mV/s, see Fig.-4, exhibit a decreased peak separation ($\Delta V_p = 47$ mV), and greatly increased 1st peak (V_{p1}) magnitude ($I_{p1}/I_{p2} = 1.56$). A small anodic oxidation peak is observed at ≈ 0.2 V.

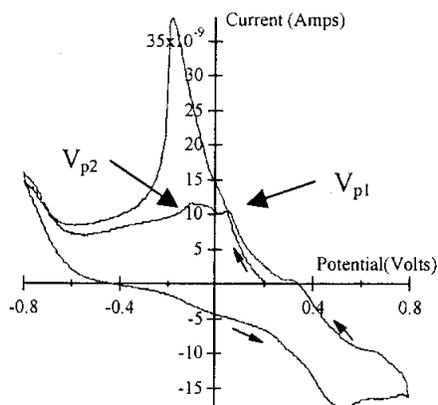


Fig.-3: 1st CV in 0.1mM adenine + 0.1 M NaCl electrolyte. Scan rate: 1mV/s.

Conclusion

These observations have not been reported for linear sweep voltammetry on gold electrodes, and illustrate that the adenine reduction process may have additional structure. This behavior is manifest by the diffusion-limited charge-carrier transport mechanisms operant at the condensate-solution interface. Thus illustrating the rationale for the slow potential scan rates employed. Dryhurst reports that adenine is not reduced via cyclic voltammetry on

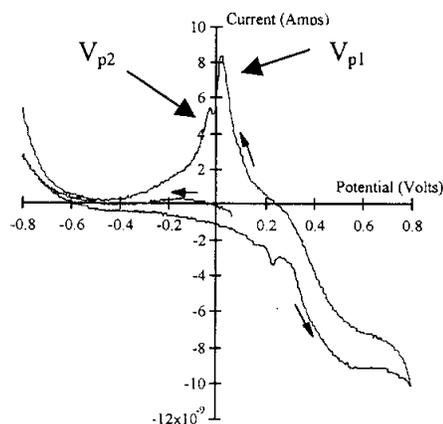


Fig.-4: CV in 0.1mM adenine + 0.1 M NaCl electrolyte. Scan rate: 0.1 mV/s.

graphite electrodes, and a single irreversible, reduction wave is observed on a dropping mercury electrode (DME).⁴ The observations for adenine represented by Fig.-2 indicate that adenine is oxidized under open circuit conditions. As shown in Fig.-3, adenine is reduced on Au in a multi-step process, each with different e^- transfer rates. As only a small anodic wave is observed on a forward scan, the reduced reaction products are stable within the time-scale of the CV at 1 mV/s scan rates, supporting Dryhurst's results on DME. The data of Fig.-4 show that the reduction products are oxidized at reduced scan rates (0.1 MV/s); consistent with the sluggish chemical kinetics observed. The current waves of Fig.-3, 4 are consistent with a diffusion-controlled $2e^-$ reduction process at the N1=C6 double bond and amine group (NH_2) of adenine. The steps in the reduction process can be determined by analyzing the reaction product(s). The results presented show that adsorbed purine bases could indeed serve as templates for the early prebiotic life forms.

References

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3. R. Srinivasan, *ibid*, 8770.
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