

## 2D Phase Transition of Viologens on HOPG Electrode Surface

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Viologen is among the most widely used electron transfer (ET) moieties in many functional systems at electrified interfaces. Highly reversible ET processes of viologens as well as ease to put them into assembled molecular structures with ET and chromatic functions have been attracting electrochemists and synthetic chemists. It is known that viologens frequently exhibit sharp spike peaks in voltammograms at Hg and other metal electrodes, and also at a HOPG electrode as found by Arihara *et al.* [1]. We assigned the spike response at a HOPG electrode (see Fig. 1 for heptyl viologen (HV)) as a two-dimensional (2D) faradaic phase transition of the first order between a gas-like expanded adsorption layer of the oxidized form of HV and a condensed monolayer of the reduced form [2-4]. Such a phase transition is governed by the strong intermolecular attractive interactions in the condensed phase.

In this paper, we describe the coexistence of the two phases in the bi-stable potential region and the effect of intermolecular interaction upon the phase transition behavior using the results of electrochemical and spectroelectrochemical measurements.

We used double potential step visible light reflectometry to track the change of the 2D fraction of condensed phase of HV on the electrode surface. The double potential step perturbation enabled us to create around 1:1 coexistence ratio of oxidized/reduced states of viologens in the bi-stable potential region, i.e. the potential region between anodic and cathodic spike peaks. However, the ratio depended on the potential at which the pre-nucleation takes place and also on the time period spent there [4].

We examined the behavior of a viologen possessing  $-\text{COOH}$  groups at the ends of the two heptyl chains (**1**: *N,N'*-bis(7-carboxy-heptyl)-4,4'-bipyridilium bisbromide). In an acidic medium, the separation of the anodic and cathodic transition potentials exceeded 120 mV as measured by potential step chrono-coulometry, indicating the presence of stronger intermolecular interaction in the condensed phase than HV. In contrast, the separation decreased in alkaline medium. Fig. 2 shows the peak potentials obtained by cyclic voltammetry at various pHs. Most likely, hydrogen bonding formation between  $-\text{COOH}$  groups of neighboring molecules on the hydrophobic HOPG surface steeply diminished in alkaline solution. The steepest decrease of the separation was observed at greater pH values than the  $\text{p}K_a$  of the carboxylic acid in solution phase. This supports the hydrogen bond

formation following the protonation of reduced form viologen molecules in the condensed phase.

One of the key factors governing the transition is the lateral interaction between the nearest neighbor molecules in the condensed phase. This in turn provides us with an opportunity to modulate the spike potentials by synthetic approach with proper design of intermolecular interaction. Regulation of the interactions will be discussed with some other examples.

### References

1. K. Arihara, F. Kitamura, K. Nukanobu, T. Ohsaka, K. Tokuda, *J. Electroanal. Chem.*, **473**, 138 (1999).
2. T. Sagara, S. Tanaka, Y. Fukuoka, N. Nakashima, *Langmuir*, **17**, 1620 (2001).
3. T. Sagara, S. Tanaka, K. Miuchi, N. Nakashima, *J. Electroanal. Chem.*, **524-525**, 68 (2002).
4. T. Sagara, K. Miuchi, *J. Electroanal. Chem.*, **567**, 193 (2004).

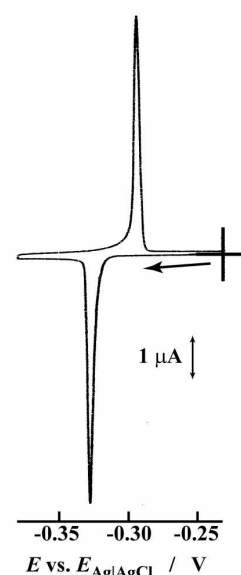


Fig. 1. Spike response at a HOPG electrode in contact with HV aqueous solution at a sweep rate of  $5 \text{ mV s}^{-1}$  at  $25^\circ\text{C}$ .

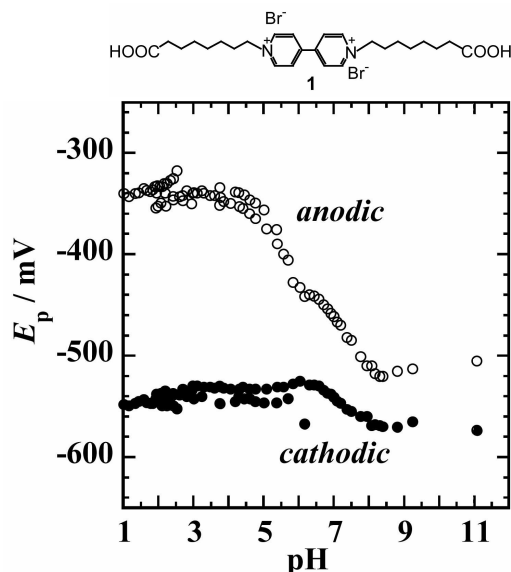


Fig. 2. pH dependence of voltammetric peak potentials of spike response at a HOPG electrode in contact with  $0.1 \text{ mM } \mathbf{1} + 0.3 \text{ M KBr}$ .