Electrochimica Acta 70 (2012) 215–227

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Voltammetry within structured liquid nanosystems: Towards the design of a flexible, three-dimensional framework for artificial photosystems

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A R T I C L E I N F O

Article history:
Received 23 December 2011
Received in revised form 19 February 2012
Accepted 13 March 2012
Available online 20 March 2012

Keywords:
Lyotropic liquid crystal
Artificial photosynthesis
Liquid nanosystem
Cyclic voltammetry
Photoelectrochemistry

A B S T R A C T

Normal lyotropic liquid crystals (in the lamellar or hexagonal phases) are investigated as a route to afford a structured, three-dimensional, quasi-biphasic framework within which electron transfer cascades may be initiated voltammetrically. For model systems, we show that these can take place through reagent partitioning between the hydrophobic and hydrophilic subphases, and illustrate how the structure and its orientation, the nature of the ionic doping of the framework, and the hydrophobicity of the redox analyte may give rise to changes in the observed voltammetric waveshape. For the case of an artificial mimic of the first few stages of Photosystem I, we demonstrate that photo-induced electron transfer is likewise affected by the orientation, and develop a system of photon efficiency of ~0.1%.

1. Introduction

Photosynthesis, the process by which solar light energy is harnessed to drive biochemical reactions, is the key to life on Earth [1–4]. Electron transfer cascades play a central role within this complex and sophisticated process, not least in allowing the transfer of electrical potential energy from the photoexcited reaction centre to long-term energy storage. In green plants, photosynthesis takes place in chloroplasts (lens-shaped structures 10 μm in diameter) [2,3], specifically within the thylakoid membrane. The whole process effects the synthesis of hexose sugars from carbon dioxide and water, through a series of “dark” reactions coupled with two light-based processes (in the so-called Z-scheme): Photosystem II actuates the oxidation of water (to produce oxygen) coupled with, ultimately, the reduction of cytochrome *f* through a series of proton-coupled electron transfer pathways in bound redox-species [2], which allows for the reduction of the freely diffusing small blue copper protein plastocyanin. This species acts to regenerate the “special” chlorophyll *a*–chlorophyll *a*′ dimer of Photosystem I (P700) through reduction of $P700^{+\bullet}$ (in a timescale of *ca.* 200 μs), which is formed after photoexcitation of P700 and electron transfer to a bound chlorophyll *a* (A_0) in a timescale of *ca.* 3 ps. Continuation of the downhill electron transfer series of Photosystem I occurs with $A_0^{-\bullet}$ reducing vitamin K_1 (A_1, phylloquinone) within 40–200 ps, followed by electron transfers to three iron-sulfur proteins and eventually ferridoxin, which allows for the proton-coupled reduction of $NADP^+$. In seeking to develop artificial mimics of the photosynthetic pathway, it is therefore essential to design supramolecular, three-dimensional ensembles of both photochemically and electrochemically active systems which are held in a proximity with good electronic couplings for fast and efficient charge transfer cascades, but, crucially, with channels for proton transfer to occur with the electron transfer [5]. Inasmuch as the engineering of such systems (dyads, triads, *etc.*) is possible [6–8], they are ultimately synthetically expensive, generally requiring the additional involvement of redox species to allow for proton translocation [9], and do not allow for the ready-probing of the underlying molecular mechanisms [8], so are not facile to optimise in terms of energy conversion efficiencies [10,11].

In this work we explore the use of normal lyotropic liquid crystal mesophases [12–15] (*q.v.* Fig. 1) formed at *ca.* 50 wt.% of surfactant in water as a “backbone” structure for the development of an inexpensive, self-reconstructing, flexible, and self-assembling soft matter-based three-dimensional, dynamic, artificial photoactive nanosystem, to a proof-of-concept, in which the surfactant pseudophase is populated with hydrophobic molecules such as chlorophyll *a* and vitamin K_1, with the aqueous subphase containing acidic electrolyte to allow facile ionic conduction, and so that the elastic properties of the surfactant system are not adversely affected by the presence of multiple types of ionic species

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doi:10.1016/j.electacta.2012.03.052

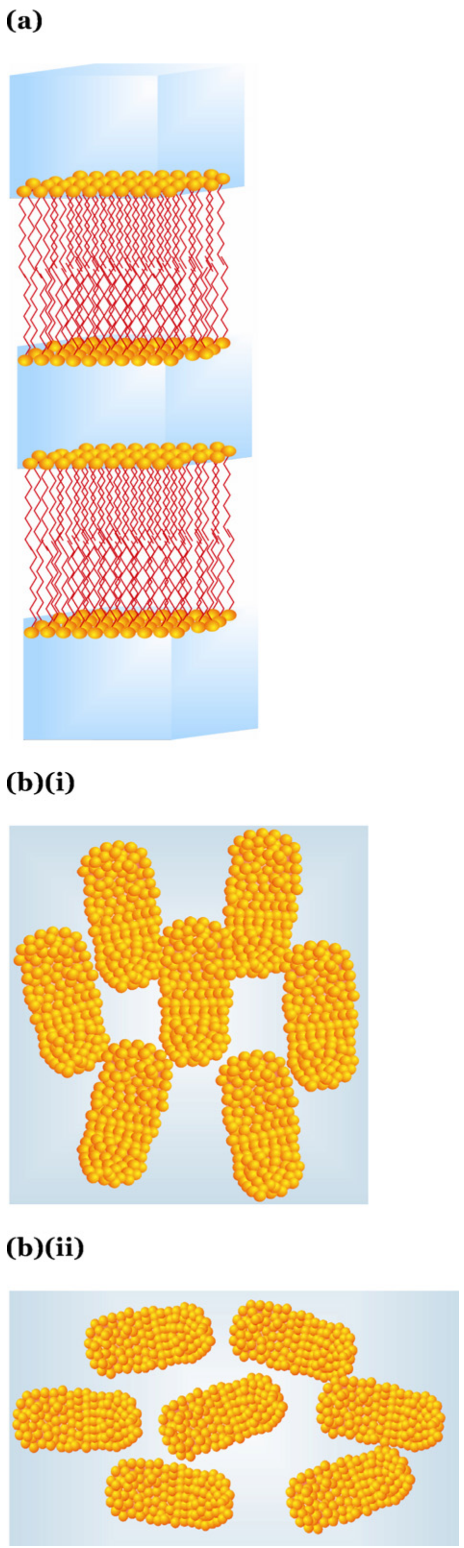

Fig. 1. Cartoon depicting (a) the L_α phase, and (b) the H_1 phase in the (i) homeotropic and (ii) homogeneous alignment referenced to the horizontal.

[16]. Indeed, the micellar palisade layer allows for charge transfer processes to occur within a medium of attractive dielectric constant ($\varepsilon_s \sim 30$) [14], which compares favourably with that of photosynthetic vesicles ($\varepsilon_s \sim 3$) [17], and the surfactant medium allows for the probing of micellar *orientation* effects on the charge-transfer process; these are seen to play a major role in both the voltammetry of model compounds, and photochemically induced electron transfer processes.

2. Theory

The use of birefringent lyotropic liquid crystal frameworks causes the possibility of anisotropic diffusion of redox analytes doped within the phase. In previous works [14,15,18], we have examined the use of ultramicroelectrodes (which probe flux in two dimensions) to determine the extent of anisotropy within such systems. In this work, however, we are concerned with effects due to the orientation of the phase relative to the electrode. Accordingly, in this work, we probe the flux within these structured liquid nanosystems within merely one dimension. This necessitates the analysis of the experimental results with the approximate theories that have been previously reported [19–21]; we detail this briefly for the case of the L_α phase in this section.

2.1. Extraction of diffusion coefficients from cyclic voltammetry within the L_α phase

If we consider the idealised case of Fig. 2a where the electrode is immersed within a lamellar phase which is aligned such that the infinite micellar bilayers are parallel with the surface of the electrode, planar, one-dimensional diffusion of any redox analyte that is free to partition between both aqueous and surfactant pseudophases to the electrode will be observed voltammetrically provided the following condition is upheld [14]:

$$\wp = \frac{r_0}{\sqrt{D_r}}\sqrt{\frac{F\nu}{RT}} \gg 1,$$

where r_0 is the electrode radius, F is Faraday's constant, ν is the voltage sweep rate, R is the molar gas constant, T is the absolute temperature and D_r is the diffusion coefficient in the direction tangential to the electrode surface. This occurs whenever *any* of the following limiting criteria is met: $r_0 \to \infty$, $\nu \to \infty$, $D_r \to 0$. In practice, this is achievable using electrodes of millimetric dimension, since the maximal size of the aqueous or surfactant subphase is between 10 and 100 Å (*viz.* five to six orders of magnitude smaller than the electrode size). The waveshape of the resulting voltammogram then follows the predictions from classical theories for voltammetry within isotropic media [14], where the peak potential depends on the ratio of the diffusion coefficients of the oxidised and reduced forms of the redox species provided the heterogeneous electron transfer kinetics are sufficiently fast (reversible). However, importantly, since the products of the electron transfer process may partition to a different extent to the reactants, with or without the further occurrence of inter-subphase electron transfer, deviations in the peak-to-peak separation to that predicted by conventional studies (~60 mV for a one-electron transfer) may occur [14]. *This means that under conditions of negligible Ohmic loss, the temporal-independence of the peak potentials is a direct marker for fast, electrochemically reversible, heterogeneous electron transfer kinetics, irrespective of the size of the peak-to-peak separation*. Thus, provided electron transfer is fast, apparent diffusion coefficients of the redox analyte may be obtained through the gradient of Randles–Sevčik plot, since, for a one-electron transfer:

$$i_p = 0.446FSc_0\sqrt{\frac{D_{ap}F}{RT}}\sqrt{\nu},$$

where i_p is the peak current, S is the electrode area, c_0 is the effective homogeneous concentration of the initial redox analyte and D_{ap} is the apparent diffusion coefficient.

This experimental transport parameter depends on two factors, under the *assumption of no transport of the surfactant framework*: