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Photoelectric properties of chlorophyll and carotene solutions in nematic liquid crystal located between semiconducting electrodes

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Abstract

The photopotential and photocurrent generation for chlorophyll *a*, β-carotene and a mixture of these pigments dissolved in nematic liquid crystal and located between transparent semiconducting electrodes were measured. Both pigments exhibit photopotential and photocurrent generation. From the photocurrent amplitudes it follows that the efficiency of electron transfer to a semiconducting electrode from β- carotene is higher than from chlorophyll *a*. The photocurrent amplitude of the pigment mixture is slightly lower than that calculated as a sum of amplitudes of pigments located in separated cells. This difference can be explained by secondary effects, such as competition between carotene and chlorophyll molecules in a process of adsorption on a semiconducting electrode. Therefore it seems that no charge transfer complexes of chlorophyll and carotene are formed in the investigated model system. © 1997 Elsevier Science B.V.

Keywords: β-carotene; Chlorophyll; Nematic liquid crystal; Photocurrent; Photopotential

1. Introduction

Carotenoids in living photosynthetic organisms work as antenna pigments and, because of effective quenching of chlorophyll triplet states, protect photosynthetic apparatus against harmful photo-oxidation [1–3]. In organisms the involvement of carotenoid pigments in the photosynthetic electron transfer has been discussed and the formation of the carotenoid cation was shown [4]. The existence of such forms was established at illumination of photosystems with inhibited water-splitting enzyme [4]. The generation of the carotenoid cations was also found, after porphyrin illumination, in the model system consisting of synthetic covalently linked carotene–porphyrin–quinone assemblies [5,6]. Photocurrent and photovoltage generation was also observed for a zeaxantin layer deposited on a metal electrode [7], showing that carotenoids are able to serve as electron donor. Interaction between chlorophyll and carotenoids depends strongly on mutual molecules' orientation and distances [8,9]. It is not easy to simulate effective singlet excitation transfer from carotenoids to chlorophyll in model systems [10,11], but it is an effective process in natural complexes [10].

In nematic liquid crystal (LC) interactions between chlorophyll *a* (Chl *a*) and β-carotene occur, as it follows from photoacoustic spectra [11], but the

Abbreviations: Chl: chlorophyll; *I*: current intensity; LC: liquid crystal; *U*: electric potential

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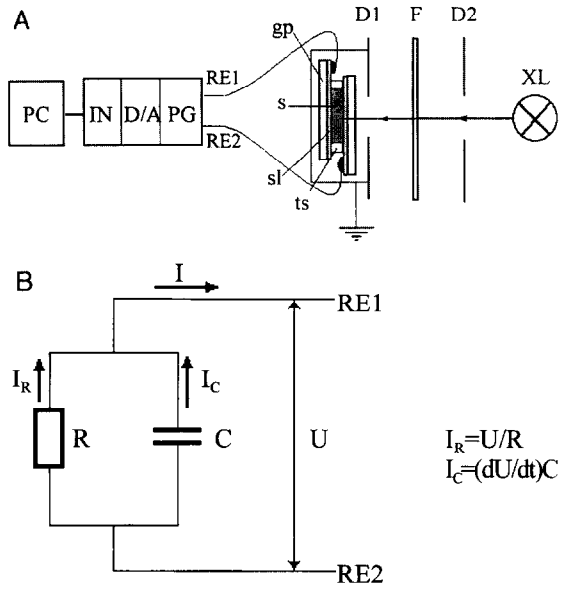

Fig. 1. (A) Diagram of cell construction and apparatus for photoelectrical measurements. PC – computer PC/AT, IN – interface, D/A – digital/analog converter, PG – programmable potentiostat/galvanostat, D1,D2 – diaphragms, F – filter, XL – xenon lamp, S – sample, gp – glass plate, sl – semiconductive layer, ts – teflon spacer. (B) Simplified electrical circuit used in calculations.

Chl fluorescence sensitized by excited carotene was not observed. The yield in thermal deactivation of energy absorbed by Chl was increasing in the presence of carotene but the molecular mechanism of these interactions is not yet clear [11]. In the present work the photoelectrochemical properties of Chl *a* and carotene located in the same matrix were compared. Also the pigment mixture was investigated in order to establish if the charge transfer process can occur between these molecules located in close proximity. The liquid crystal solvent simulates several properties of biological membranes [12,13]. Such a solvent influences the charge transfer reactions as it follows from the observation of photo-induced intra-molecular electron transfer between covalently linked porphyrin–quinone systems embedded in liquid crystals. Such effects were investigated by time resolved EPR [14]. Liquid crystal (LC) solvent enhanced also the photocurrent and photovoltage generation in a photoelectrochemical cell with chlorophyll [15].

2. Material and methods

Chl *a* was purified chromatographically according to the method described in [16]. The β-carotene (Fluka AG, Chem. Fabrik CH-9470 Buchs) was used without further purification. Pigments were dissolved in a nematic liquid crystal mixture of p-methoxybenzylidieno–p-butylaniline (MBBA) + p-ethoxybenzylidieno–p-butylaniline (EBBA) (3:2). Both liquid crystals (from E. Merck, Darmstadt) were used without purification. LC samples with Chl *a* $1.0 \cdot 10^{-3}$ M and β-carotene $0.5 \cdot 10^{-3}$ M concentrations were prepared. The solution of pigment mixture in LC of the same concentrations of Chl *a* and β-carotene was also prepared. The solutions of pigments and their mixture were located in electrochemical cells with windows from conducting glass (In_2O_3 layer on a glass plate). The construction of the cell and arrangement used in the measurements of photovoltage and photocurrent are shown in Fig. 1. The fluorescence and fluorescence excitation spectra were recorded with the arrangement constructed in our laboratory, the absorption spectra with a Zeiss Specord M40.

3. Results and discussion

Fig. 2 shows the absorption spectrum of both pigment mixtures which is the exact superposition of

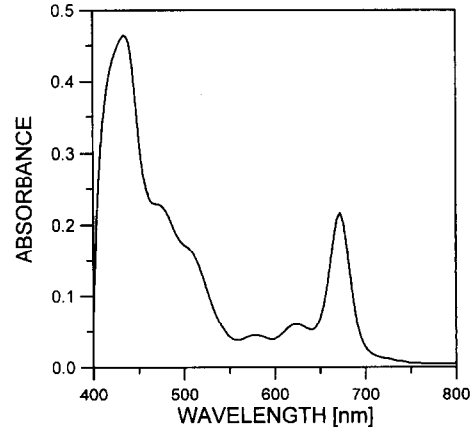

Fig. 2. Absorption spectrum of Chl *a* and β-car mixture in LC. Pigment concentrations: $c_{Chl} = 1.0 \cdot 10^{-3}$ M, $c_{car} = 0.5 \cdot 10^{-3}$ M (for all present results).

Chl *a* and β-carotene spectra measured in separated cells. It suggests that the ground state complexes of both pigments are not formed in LC mixture. The Chl *a* located in LC is not aggregated because of strong interaction between LC and pigment molecules [11]. Similar conclusions follow from not shown fluorescence spectra.

As it follows from absorption spectra the β-carotene in the investigated samples is mostly in mono dispersed form. Previously [11] β-carotene was in some extent crystalline. Now, by the mixing of diluted pigment solution with LC and slow evaporation of chloroform mono dispersed carotene in LC solution was obtained. The normalized excitation spectra of 680 nm fluorescence of Chl alone and pigment mixture are very similar, but in the carotene absorption region (450–550 nm) the excitation spectrum intensity in a pigment mixture is slightly lower than for Chl alone. This is due to the inner filter effect: carotene molecules are absorbing part of the light. The course of fluorescence excitation spectra suggests that similarly as in previous work [11] the excitation energy transfer (ET) from excited carotene to chlorophyll is not occurring.

The fluorescence spectra recalculated on the unit of absorption and the unit of excitation energy measured for Chl alone and for the pigment mixture recorded at 420 nm and 535 nm excitation show also lack of the measurable ET from the excited singlet of carotene to Chl.

Typical kinetics of photopotentials generation and decay are shown in Fig. 3.

In darkness, all samples exhibit an open-circuit potential difference U_0 and in short-circuit connection a dark current I_0. Both values are changing with time: U_0 slowly, I_0 much faster. The values of U_0 and I_0 are reaching their plateaus in different times for the various cells. The photopotential changes were measured in a region of the saturation of these dark effects (Fig. 3) and just after cell connection.

In a second case the measured kinetics are the superposition of the value of the potential $U_0(t)$ taken at a proper time after the moment of cell connection in a circuit and of the increase in potential value due to sample illumination. The light-generated changes in potential values for Chl *a*, β-carotene and the pigment mixture have different amplitudes. For all samples the photopotential increase is

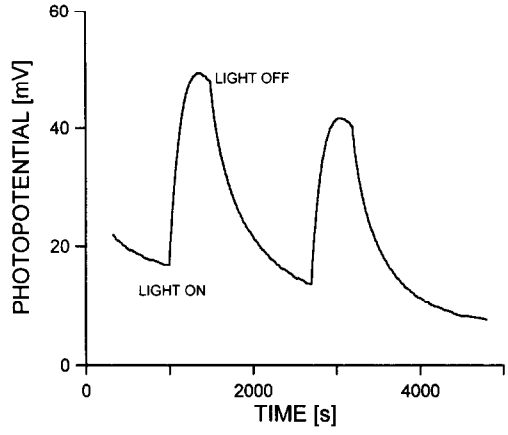

Fig. 3. Photopotential kinetics for pigment mixture in LC.

faster than the decay. The maximal value of the potential amplitude is increasing with increase in pigment concentration as well as with increase in light intensity. Photopotential kinetics were also changed by the application of the external potential to the dark cell, prior to the photopotential generation experiment.

This can suggest the occurrence of the two following effects:

1) the reorientation with respect to the electrode of the LC molecules due to electrical field application and consequently the pigment reorientation by the 'guest–host' effect, and/or

2) the direct perturbation by the field of the charged molecules adsorbed on the electrode and the double layer of ionic species (Helmholtz double layer) formed near to semiconducting electrodes.

The second supposition is more plausible, because the LC used in this work has negative dielectric anisotropy; therefore their molecules are oriented perpendicularly to the direction of the electrical field applied. Because the initial orientation of LC molecule is near to the parallel to the plane of the cell windows, the application of the potential can only slightly improve the degree of the LC orientation.

Fig. 4 presents the kinetics of the photocurrent. The direction of the photocurrent shows that photoelectrons are flowing in a circuit from the illuminated to the dark electrode. The kinetics of photocurrent generation are similar for the Chl solution, for

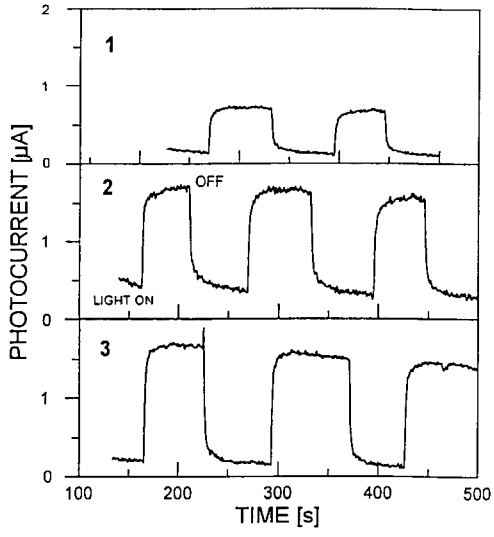

Fig. 4. Kinetics of photocurrents for pigments in LC: 1 – Chl *a*, 2 – β-car, 3 – pigment mixture.

carotene and for the pigment mixture. The maximal photocurrent value is increasing with increase in the light intensity, but the ratio of the current amplitudes is lower than the ratio of the light intensities. The number of quanta in einsteins incident on the cell surface in 1 s is of the order of 10^{-7} cm^{-2} s^{-1} whereas the molar concentration of pigments is of order 10^{-3} M. Taking into account the kinetics of pigment ionization and recombination (of the order of a ms) one can expect the occurrence of saturation effects. The increase in light intensity cannot improve the photopotential generation when practically all pigment molecules located near to the electrode surface are already excited or ionized. As it follows from our previous result [20] only the thin layer of sample located near the electrode is active in photopotential generation. Because the thickness of this layer is not exactly known, it is not easy to evaluate a cross-section for photopotential generation at various light intensities and pigment concentrations.

Because of faster saturation of time changes in I_0 than changes in U_0, photocurrents can be easier quantitatively interpreted than photopotentials. The amplitude of photocurrent generation recalculated for the same dye concentration and light conditions is higher for β-carotene than that generated in a cell with Chl *a* (Fig. 4). The sum of both amplitudes is higher than that observed in the pigment mixture. This can be due to shielding of part of the electrode surface by Chl molecules against the carotene adsorption. It follows from the results obtained for separated pigments that the yield of redox reaction at the semiconductor electrode/sample interface for carotene is higher than that for Chl *a* molecules. Therefore in a pigment mixture, when part of the electrode surface could be shielded by adsorbed Chl, a lower number of carotene molecules may be located near the surface of the cell window than in the cell with carotene alone. The yield of electron transfer in this case is evaluated for the same pigment concentration. It is also not possible to exclude the formation of some carotene–chlorophyll aggregates but this effect has to be inefficient as it follows from the spectra of the pigment mixture. Fig. 5A shows the current–voltage dependence $I(U)$ (voltammograms) for the investigated samples at three speeds of voltage changes (5 mV/s, 10 mV/s and 20 mV/s).

The capacitance of the electrochemical cell filled only with LC calculated under the supposition of random LC orientation [12] is about 1.1 nF for our cell geometry.

Voltammograms such as the one in Fig. 5, obtained by application of the cyclic voltammetry technique, allow one to investigate the redox reactions at the semiconductor electrode/sample interface [17]. The shape of the observed voltammograms and the value of the open circuit voltage (U_0) can be interpreted in terms of the redox reaction occurring at this interface. The voltammograms presented in Fig. 5 were taken in darkness at so-called linear sweep, i.e. when the applied voltage (U_p) increases linearly with time ($dU_p/dt = \text{const}$). They give information about electrical properties of the pigmented cells in the dark. Most efficient redox compounds exhibit strong asymmetry of $I(U)$ dependence and high U_0 [17]. In our system the addition of β-carotene to the Chl solution in LC changes the shape of the $I(U)$ curve, which became similar rather to that of carotene alone than that of the Chl *a* solution (Fig. 5B).

From the $I(U)$ dependence the values of cell capacity under simplified suppositions (explained in Fig. 1B) are calculated and presented in Fig. 6. Under the used supposition (Fig. 1) the voltammogram loop still exists and it is possible to evaluate the parameters of the cell. The capacitance of the

pigmented cell obtained from the $I(U)$ curve is three orders higher than that calculated from cell geometry and LC dielectric properties.

The difference is due to the spatial charge distribution inside the 'cell-capacitor'. The pigment cations are adsorbed on the electrode surface and at some distance from this electrode a Helmholtz double layer is formed. This is a situation similar to the one observed for polymer-pigment complexes in an electrochemical cell [18]. At high speed of voltage changes (20 mV/s) the cells with various pigments exhibit similar C: about 3 μF. For lower speeds the

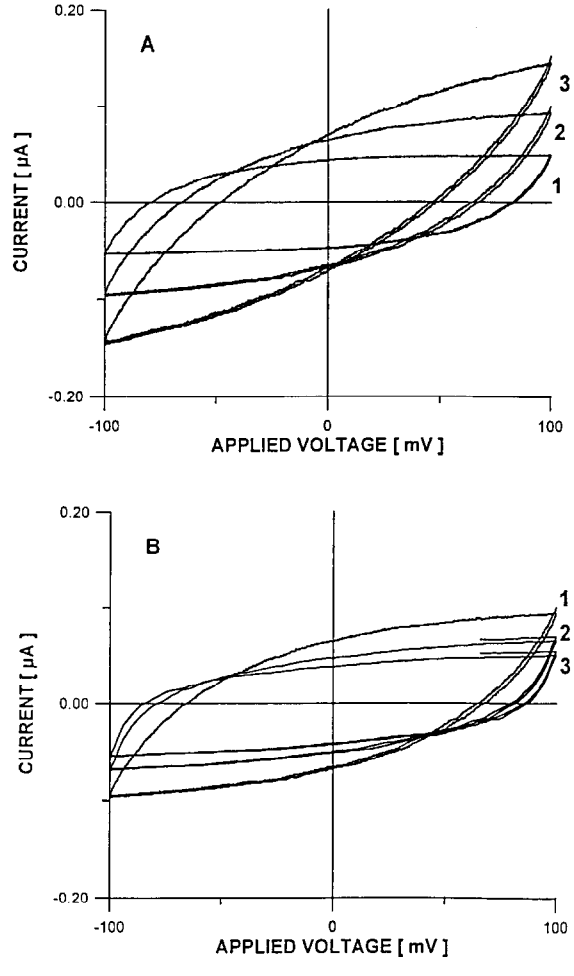

Fig. 5. (A) Current–voltage dependence $I(U)$ for Chl a in LC at three speeds of voltage changes: 1: $dV/dt = 5$ mV/s, 2: $dV/dt = 10$ mV/s, 3: $dV/dt = 20$ mV/s. (B) Current–voltage dependence $I(U)$ at $dU/dt = 10$ mV/s for pigments in LC: 1 – Chl a, 2 – β-car, 3 – pigment mixture.

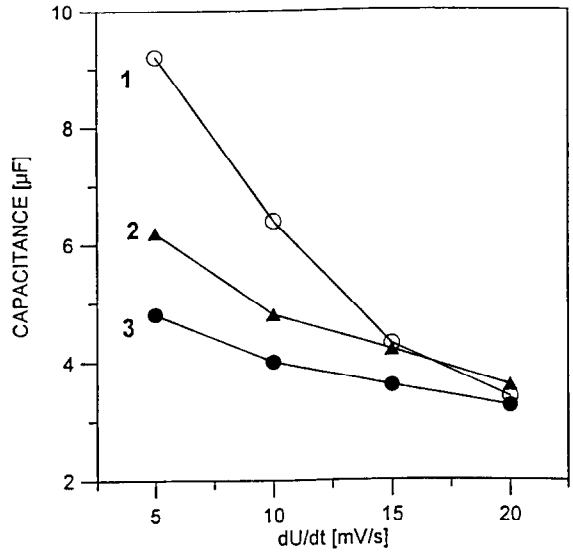

Fig. 6. Capacitance vs. speed of potential change dU/dt for pigments in LC: 1 – Chl a, 2 – β-car, 3 – pigment mixture.

capacities for various samples are different. As was shown previously [13], the dielectric constant of a photoelectrochemical cell filled with a chlorophyll solution in liquid crystal depends strongly on the frequencies applied for frequencies lower than 50 Hz. This effect, much stronger than that for unpigmented liquid crystal, is due to the perturbation of the liquid crystal matrix and also the distribution of charge in a cell by pigment. The perturbation depends on the type of pigment and its concentration [13]. The strongest increase is observed for Chl alone, the lowest for the pigment mixture (Fig. 6). The resistance of the cell is very high: of MΩ order. This shows that processes responsible for the current generation in a short-circuited cell are related to the interaction of dye molecules located near windows with a semiconducting electrode. The resistances are also different for various samples and dependent on dU/dt. The influence of the pigment concentration on electrical properties of the cell was also observed previously [18]. It is due to the formation of a charged layer in the cell [19]. The asymmetry of electrodes in the dark is formed by their slightly different properties. After illumination asymmetry is increasing because of the light gradient. The change in the side of the cell illumination (from the initially illuminated electrode 1 in Fig. 1 to the second elec-

trode) causes the diminishing of the reached photocurrent amplitude. This means that illumination causes some formation of the charge distribution in a cell. The $I(U)$ dependencies for illuminated and dark cells are mutually shifted (not shown).

It is possible that the difference in mobilities of carriers, produced near the illuminated electrode, can have influence on photocurrent and photopotential generation.

On the basis of the presented results one can conclude that:

1. At the same pigment concentrations and other experimental conditions carotene is more efficient in photocurrent and photopotential generation than chlorophyll *a* molecules.

2. For the mixture of pigments photocurrent is only slightly lower than the sum of photocurrents measured for separated pigments. This suggests that the formation of the mixed Chl–carotene aggregates or charge transfer complexes is inefficient in the investigated solvent.

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