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Action spectra of the photopotential generation for pigment and dye solutions in nematic liquid crystals located in the electrochemical cell

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Abstract

The method of measurements of the action spectra of photopotential generation using a modulated acting light beam was elaborated and applied to two systems: the solutions of stilbazolium merocyanines and to the mixture of chlorophyll *a* and luteine. Both types of samples were dissolved in nematic liquid crystal and located either between two semiconducting electrodes, or between a transparent gold electrode and a semiconducting electrode. By changing the frequency of light modulation or the phase shift between a modulated light beam and a measured photopotential signal, information about the kinetics of photopotential generation is obtained. The free base and protonated merocyanine forms exhibit different kinetics of potential generation. The amplitude of the photopotential of the chlorophyll and luteine mixture is higher than the sum of the amplitudes of the photopotential of these pigments located in separated cells. In a cell with two semiconducting electrodes, the light gradient (e.g., different illumination of front and back electrodes due to light absorption) plays an important role in photopotential generation. © 1998 Elsevier Science S.A.

Keywords: Action spectra; Chlorophyll; Luteine; Merocyanine; Photopotential

1. Introduction

Several systems are proposed for the conversion of light energy to electrical energy [1–3]. Some of the proposed systems which contain parts of living organisms simulate processes which occur in illuminated pigmented biological membranes [4]. Previously [5–7] the photocurrent and photopotential generation in model systems was investigated. But when using steady-state illumination, the measurements of photopotential were not precise because of the perturbation of the results by potential obtained after the connection of the cell in darkness which was not stable at the time [8]. These changes are due to some chemical processes which the electrodes and the sample undergo. Therefore a new arrangement for the measurements of the action spectra of photopotential generation at modulated acting light was elaborated.

The arrangement was applied to the investigation of the photopotentials of two types of samples: the stilbazolium merocyanines and the chlorophyll–luteine mixture located in nematic liquid crystals (LC). Merocyanines occur in LC in the protonated and the free base forms. In the first type of samples, we wanted to verify if the proposed method was useful in distinguishing the photoelectrical process occurring in various kinetics, because it is known [9] that such effects occur with different kinetics for neutral and charged dye molecules. The second type of sample is important from the biological point of view [10,11]. The carotenoids and chlorophyll interactions have been our subject of interest for an extended period and have been investigated in model systems and in organisms [12,13].

2. Experimental

Fig. 1 shows the apparatus used for the photopotential action spectra measurements. The contributions from the slow processes of photopotential generation can be distinguished from quick photoelectrochemical processes by recording the action spectra at various modulation frequencies of acting light (ν).

The amplitude of photopotential depends on the frequency of light modulation when the time of the generation or the decay of photopotential is comparable to the dark–light periods applied in the modulated beam.

Similarly, the change in the shape of the action spectrum with the change in the phase shift (ϕ) between the modulated light beam and the measured photopotentials shows that the contributions to photopotentials with various kinetics occur

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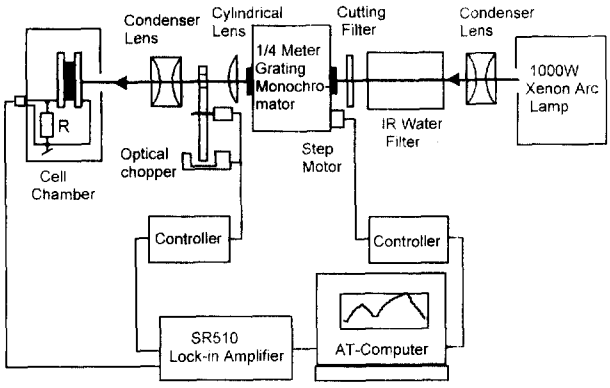

Fig. 1. Scheme of arrangement used for the photopotential action spectra measurements.

in various spectral regions. Two types of cells were used: the first with one semiconducting (In_2O_3) electrode and a second transparent gold electrode; the second with two semiconducting electrodes [5–7].

Two stibazolium merocyanines were used: 1-(11′-hydroxyhexyl)-4-/(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)ethylidene/-1,4-dihydropyridine and 1-(6′-hydroxyhexyl)-4-/(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)ethylidene/-1,4-dihydropyridine denoted as mero-E and mero-D, respectively.

Both merocyanines were obtained from Professor Ilona Gruda (Trois Rivieres, Canada).

Chromatographically purified chlorophyll (Chl) *a* [14] and luteine extracted from nettle leaves, as well as their mixture, were also investigated. Two types of nematic liquid solvents were used without further purification: mixture *p*-methoxybenzylidieno-*p*′-butylaniline (MBBA) + *p*-ethoxybenzylidieno-*p*′-butylaniline (EBBA) (3:2) and K15 (*p*-pentyl-*p*′-cyanobiphenyl) all liquid crystals from E. Merck, Darmstadt.

3. Results

We compare the efficiency of photopotential generation in various merocyanine forms considering the photopotential amplitude (Fig. 2) recalculated on the same unit of absorption (Fig. 3) and the number of incident quanta. Such recalculations proves that in most solvents the protonated form is much more efficient than the free base form. For example: with Mero-D in MBBA + EBBA (Fig. 2A curve 1), the ratio of protonated to free base forms efficiencies is about 28 and for Mero-E in K15 (Fig. 2B curve 2) about 25. In this comparison data for similar experimental conditions are taken. The variation in the type of dye, type of solvent and in the modulation frequency and/or the phase between acting light and measured signal changed this ratio, which shows that the photopotential kinetics of these two forms are different. For example in a case of Mero-E at $\phi = -61°$ for $\nu = 4$ Hz this ratio is 13 whereas for $\nu = 6$ Hz it is 25 (Fig. 2B curves 1 and 2, respectively).

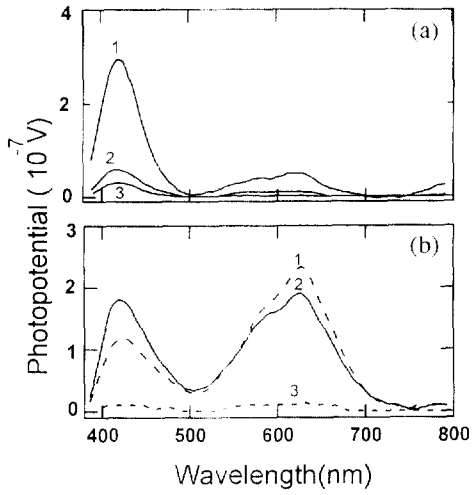

Fig. 2. Photopotential generation action spectra: (A) Mero-D in MBBA + EBBA at $\phi = -44°$. (1) $\nu = 6$ Hz, (2) $\nu = 40$ Hz, (3) $\nu = 80$ Hz. (B) Mero-E in K15 at $\phi = -61.2°$. (1) $\nu = 4$ Hz, (2) $\nu = 6$ Hz, (3) $\nu = 80$ Hz.

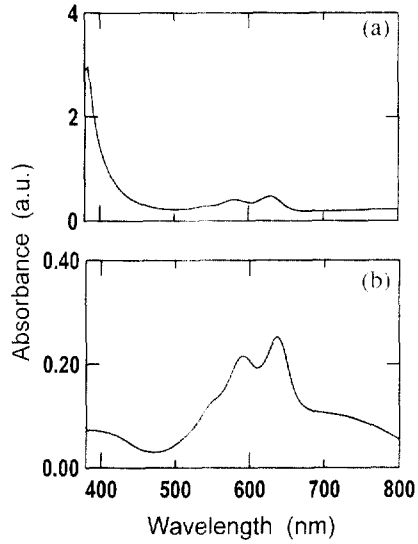

Fig. 3. Absorption spectra for: (A) Mero-D in MBBA + EBBA, (B) Mero-E in K15 (Concentration = 10^{-3} M/l).

Previously [9] it was shown that protonated form in electrochemical cells give different kinetics of photocurrent generation than the neutral form of dyes. These changes show that the various forms of dye exhibit photopotential generated with different speed. The comparison of absorption and photopotential spectra proves that LC is either not a source of photoelectrical effect, or that this effect is much lower than that related to the dye. This finding is in agreement with our previous results [7]. The MBBA + EBBA exhibit strong absorption in the 400 nm region, but the photopotential action spectrum reaches its maximum at 430 nm due to the dye absorption.

Figs. 4 and 5 show the absorption and action spectra of photopotential measured for the solution of Chl *a*, luteine and their mixture dissolved in LC (K15) and located between semiconducting and metal electrodes.

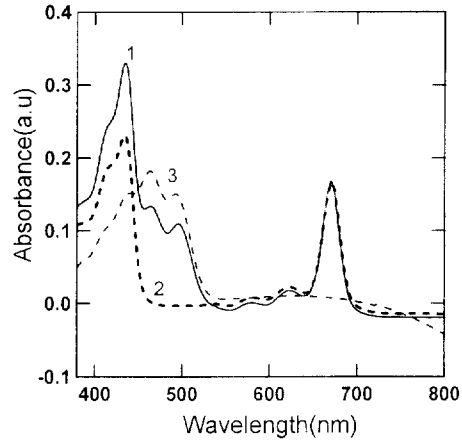

Fig. 4. Absorption spectra: (1) Chl *a* + luteine in K15, (2) Chl *a* in K15, (3) uteine in K15 (Concentration = 10 $^{-3}$ M/l).

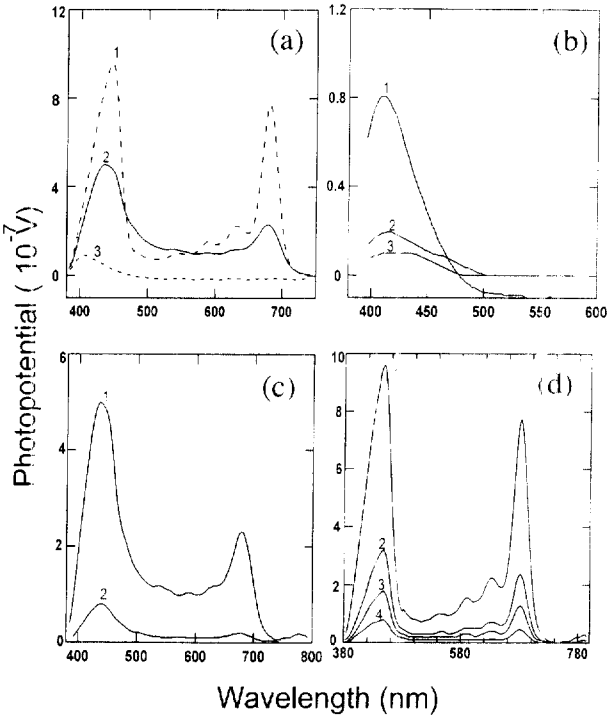

Fig. 5. Photopotential generation action spectra: (A) at ν=6 Hz for: (1) Chl *a* + luteine in K15, (2) Chl *a* in K15, (3) luteine in K15. (B) for luteine in K15: $\phi = -44°$, (1) ν=6 Hz, (2) ν=40 Hz, (3) ν=80 Hz. (C) for Chl *a* in K15: $\phi = -44°$, (1) ν=6 Hz, (2) ν=80 Hz. (D) for Chl *a* + luteine in K15: $\phi = -44°$, (1) ν=6 Hz, (2) ν=40 Hz, (3) ν=80 Hz, (4) ν=120 Hz.

The absorption of the pigment mixture is approximately the sum of the absorption of Chl *a* and luteine measured in separated cells. This additive reveals that the ground state complexes of these pigments are not formed. Fig. 5A suggests that luteine alone is not very effective in photopotential generation, but changes the photopotential amplitude of the pigments mixture. The ratios of the photopotential amplitudes recalculated on the same amount of absorbed quanta amplitudes of photopotentials are for Chl *a*:Chl *a* with luteine:luteine equal to 3.0:5.1:0.6. It reveals that the mixture of pigments exhibit much higher photopotential amplitude than the sum of amplitudes measured for the pigments in separated cells. Thus, the interactions between pigments must be responsible for this change. These interactions promote the ionization of dyes.

From Fig. 5B and C, it follows that for both pigments photopotential amplitude decreases with the increase in modulation frequency. This was predictable because at the rather slow kinetics of photopotential generation [5–9] in the short light period the amplitude increases by small degree. The effect is far from saturation. A more interesting effect is presented in Fig. 5D, which shows the dependence of photopotential on frequency modulation in the case of pigment mixture. As it follows from Fig. 6 calculated on the ground of the spectra from Fig. 5D; the ratio of Soret (A) to red band (B) photopotential amplitude changes for such samples with the frequency of light modulation. As it follows from absorption spectra (Fig. 4) in a Soret region the luteine band is to some extent superimposed on the Chl band. The result presented in Fig. 6 shows that the kinetics of potential generation are different for both pigments. Fig. 7 presents 'a light gradient effect' for Chl *a* and Chl *a* with luteine mixture. The light gradient effect can be investigated by the comparison of the results obtained from the illumination of the cell from the front and back sides. The sample is located between two semiconducting electrodes. One of them, is grounded in both experiments. The scheme of electrical connections is shown in Fig. 7. As shown previously [9], the sign of the signal for the cells with both semiconducting electrodes changes from cell to cell, because the electrodes are never identical. We changed the side of illumination without changing the electrical circuit for the same cell. After this change the light which reached the electrode at which the space charged layer is larger (1), has to cross the sample and is partially absorbed. As a result of the change of the illumination from (1) to (2) electrode, the sign of photopotential is reversed. To measure positive amplitude the phase (ϕ) has to be shifted by 180°. These experiments show the that light gradient in measured

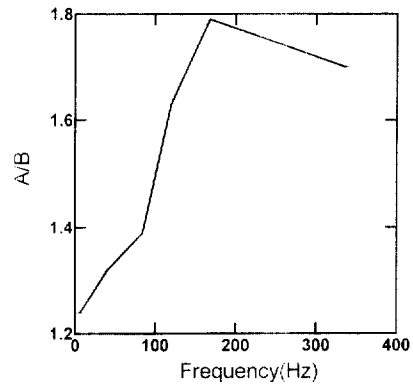

Fig. 6. The ratio of photopotential amplitudes measured of Soret (A) and at red (B) bands for various frequencies of light modulation for Chl *a* and luteine mixture.

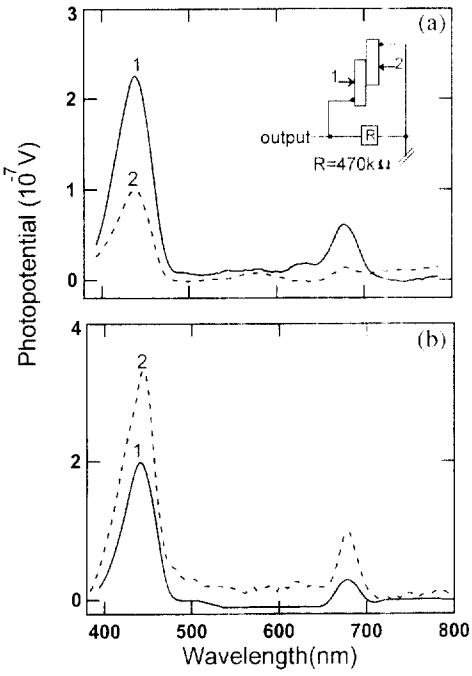

Fig. 7. Photopotential action spectra for a cell illuminated from different sides of semiconducting electrodes. Scheme of electrical connections is shown in a figure. Curve (1): illumination from a side of first (1) electrode. Curve (2): illumination from a side of grounded (2) electrode: (A) Chl *a* in K15: curve (1) $\phi = -62.1°$, $\nu = 6$ Hz; curve (2) $\phi 155.3°$, $\nu = 6$ Hz. (B) Chl *a* with luteine in K15: curve (1) $\phi = -61.8°$, $\nu = 6$ Hz; curve (2) $\phi 113°$, $\nu = 6$ Hz.

cells play a more important role than the differences in the properties of electrodes. The measured effect occurring within a short time after the beginning of illumination. At steady state illumination, the differences in electrode properties was dominating 'light gradient' effect [9,15,16]. Since the light gradient is used for the explanation of photopotential generation in chloroplasts [5,17], this result shows that our model can simulate the photoelectrical properties of chloroplasts.

4. Conclusions

(1) It is shown that by using modulated light with lock-in amplifier, it is much more possible to establish the action spectra of photopotential generation and distinguish the forms of dyes exhibiting the various kinetics of potential generation.

(2) The mixed ground state aggregates of Chl *a* and luteine are not formed, but the presence of luteine in the Chl *a* solution in LC changes the kinetics of photopotential generation in a spectral region in which the spectra of both pigments are overlapped.

(3) The kinetics of Chl *a* photopotential generation are faster than those of luteine located in the same LC.

(4) The amplitude of photopotential generation recalculated on the same amount of absorbed quanta are larger for Chl *a* than for luteine. In a pigment mixture the effects are not additive. The presence of luteine enhanced the photopotential generation.

(5) The light gradient, that is the different illumination of both semiconducting electrodes, plays an important role in photopotential generation.

5. Nomenclature

EBBA, *p*-ethoxybenzylidieno-*p'*-butylaniline
MBBA, *p*-methoxybenzylidieno-*p'*-butylaniline
K15, *p*-pentyl-*p'*-cyanobiphenyl
Mero-D, 1-(6'-hydroxyhexyl)-4-/(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)ethylidene/-1,4-dihydropyridine
Mero-E, 1-(11'-hydroxyhexyl)-4-/(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)ethylidene/-1,4-dihydropyridine

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