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Electrical properties of phosphatidylcholine bilayers containing canthaxanthin or β-carotene, investigated by electrochemical impedance spectroscopy

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ABSTRACT

Electrochemical impedance spectroscopy technique was applied to study bilayer membranes formed with egg yolk phosphatidylcholine containing as an additional component one of two carotenoid pigments: canthaxanthin or β-carotene. The results show that both carotenoids present in the lipid membranes at relatively low concentration modify significantly electrical capacitance and electrical resistance of the membranes. Domain structures appear as a result of interactions between components within analyzed bilayers. The equilibrium of domain formation can explain the deviation from the additivity rule. This equilibrium was described by mathematical equations as well as verified experimentally. Moreover, the surface area of domains was calculated and their stoichiometry was proposed.

1. Introduction

Electrochemical Impedance Spectroscopy (EIS) is an experimental procedure and important technique to evaluate the underlying characteristics of biosensors, body fluids, electrochemical fuel cells, and electronic circuits. This measurement technique dates back to the late nineteenth century and is associated with investigations performed with the usage of the Wheatstone bridge of dielectric permittivity of aqueous solutions, organic liquids and oxides [1–4]. In the late 40s of the last century, the application of EIS for the measurement of electrochemical systems resulted in the appearance of the reports presenting the concept of an electrical equivalent circuit of a simple electrode reaction [5,6]. The scheme known as “Randles circuit” is now often taken as a base in the analysis of impedance results.

In recent years, electrochemical impedance spectroscopy has been applied in the studies of bilayers and self-assembling monolayers [7], which are useful model systems to study basic interaction mechanisms that are responsible for the structure and function of biological membranes. The simple composition of artificial membranes in contrast to the complex mixture of lipids and proteins in biological ones facilitates a detailed examination of a single membrane function, e.g. ion transport [8]. The electrical capacitance and electrical resistance of the membranes are important parameters to analyze using EIS. They can be treated as independent parameters defining the membranes or as the auxiliary magnitudes enabling determination of other membrane parameters, such as potentials or electrical charges. Impedance spectroscopic studies represent a dynamically developing field of science, and possess interesting research purposes and practical applications. Performing this kind of studies, being on the borderline with electrochemistry and biology, requires a comprehensive knowledge of both of these fields. For the proper interpretation of the obtained results, a precise planning and execution of such experiments, together with deep knowledge of impedance spectroscopy, is required.

Among the unsaponifiable lipids of plants and animals are found representatives of a group of pigments (light yellow to purple) known as the carotenoids. These substances are present in small amounts in nearly all higher plants and in many microorganisms (e.g. red and green algae, fungi, and photosynthetic bacteria); they are probably also present in all animals [9]. Most of the natural carotenoids are oxygenated compounds and may be classified as derivatives of the hydrocarbons lycopene or α-, β- or γ-carotene, for example canthaxanthin is an oxygenated derivative of β-carotene (see Fig. 1). Nonpolar β-carotene (βC) is probably the most abundant carotenoid in nature and has multiple and diverse physiological functions [10]. Polar canthaxanthin (CAN) has been investigated extensively in recent years, mainly because of its application as a food colorant and a component of sun creams and pills [11]. There is increasing interest in the role of βC, CAN and other carotenoids in human chronic diseases, including cancer [12], retinal

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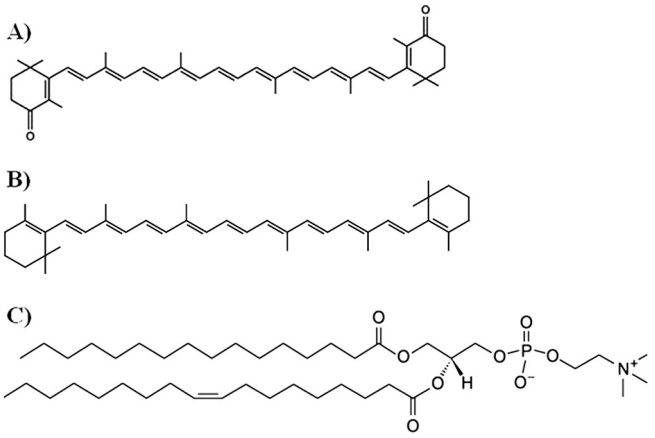

Fig. 1. Chemical structure of CAN (A), βC (B), and PC (C).

dystrophy [13], retinopathy [14] or aplastic anemia [15].

It is clear that, as membrane components, the carotenoids must be able to fit into this well-organized structure with the correct position and orientation. Hereby, the better understanding of the physicochemical properties of carotenoids and their interactions with lipids is necessary to clarify the exact mechanism of their function in biological membranes. Numerous studies using the model systems have showed several effects of carotenoids on the structure and dynamics of lipid membranes e.g. nuclear magnetic resonance [16], light scattering [17], differential scanning calorimetry [18] or electron spin resonance [19]. In spite of such a broad experimental approach, the behavior of carotenoids, especially CAN and βC, in biological membranes is not unequivocally determined [20].

Based on our experience in studying the effect of various natural components [e.g. 21–23] on phospholipid bilayers, in this study we applied the electrochemical impedance spectroscopy method as a complementary to experimental techniques to investigate the effect of carotenoids on electrical properties of lipid membranes and molecular organization of carotenoid molecules in the lipid phase. We selected CAN and βC as the pigments with and without a functional group on the β-ionone ring, respectively. As lipid we have used phosphatidylcholine (PC, see Fig. 1) because it is present in biological membranes and it fulfills essential functions in lively organisms. Our results show the formation of the PC-carotenoid domains in bilayers containing < 0.03 M fraction of a carotenoid. The determination of the area occupied by one domain is the final research result.

2. Theory

During formation of a mixed two-component bilayer, the individual components (denoted by 1 and 2) may or may not form another compound.

The model, which has been described in full detail previously [22], assumes that in the case where the membrane components do not form chemical compounds, their interaction might be described by the equation based on the additivity of electric capacity [22]:

$$C_m = C_1 c_1^s S_1 + C_2 c_2^s S_2 \tag{1}$$

in which:

$$x_1 = \frac{c_1^s}{c_1^s + c_2^s} \tag{2}$$

$$c_1^s S_1 + c_2^s S_2 = 1 \tag{3}$$

$$x_1 + x_2 = 1 \tag{4}$$

where:

C_m [μF cm^{-2}] the measured capacitance of the membrane;
C_1, C_2 [μF cm^{-2}] the capacitances of the membrane built by components 1 and 2, respectively;
c_1^s, c_2^s [mol m^{-2}] the surface concentrations of components 1 and 2, respectively, in the membrane;
S_1, S_2 [m^2 mol^{-1}] the surface areas of 1 mol of the membrane formed from components 1 and 2, respectively;
x_1, x_2 the molar fraction of components 1 and 2, respectively.

Eliminating c_1^s and c_2^s, it can be stated that:

$$(C_m - C_1)x_1 = -\frac{S_2}{S_1}(C_m - C_2)x_2 \tag{5}$$

The spatial regionalization of components occurs during formation of a two-component membrane, leading to the creation of lipid domains, which are characterized as membrane regions of diverse chemical character, structure, and functions. Assuming that every molecule of component 2 is surrounded by a certain, possible to determine, quantity of component 1, the equilibrium of domain formation (compound 3) might be characterized by electric capacity [24,25]:

$$C_m = C_1 c_1^s S_1 + C_3 c_3^s S_3 \tag{6}$$

here:

$$x_1 = \frac{c_1^s}{c_1^s + c_3^s} \tag{7}$$

$$c_1^s S_1 + c_3^s S_3 = 1 \tag{8}$$

$$x_1 + x_3 = 1 \tag{9}$$

where:

C_3 [μF cm^{-2}] the capacitance of the membrane built of compound 3;
c_3^s [mol m^{-2}] the surface concentration of compound 3 in the membrane;
S_3 [m^2 mol^{-1}] the surface area of 1 mol of the membrane formed from compound 3;
x_3 the molar fraction of compound 3.

Elimination of c_1^s and c_3^s yields the equation:

$$C_m = \frac{C_1 S_1 + (C_3 S_3 - C_1 S_1)x_3}{S_1 + (S_3 - S_1)x_3} \tag{10}$$

Eq. (10) is a quotient of polynomials. Dividing the numerator of the quotient by its denominator gives a series of increasing exponents of the power of molar fraction, x_3. Moreover, considering two first terms of the series leads to the linear expression, that is valid at low molar fractions (for $x_3 \to 0$):

$$C_m x_3^{-1} = C_1 x_3^{-1} + (C_3 - C_1)S_1^{-1} S_3 \tag{11}$$

The equations above (Eqs. (1)–(11)) can be derived in an analogous manner, taking into account the conductance (instead the capacity).

For a bilayer membrane built of lipid and carotenoid, domain formation was assumed to be the explanation for deviation from the additivity rule. Model curves were constructed using calculated parameters such as surface areas of lipid and pigments, as well as capacitances of molecules and domains. The accuracy of the models was verified by comparison to experimental results.

3. Experimental section

3.1. Materials

The compounds used in experiments, namely L-α-phosphatidylcholine, β-carotene, and canthaxanthin were the products of high purity (≥ 99.0%, ≥ 97.0%, 97.5%, respectively) purchased from Sigma-Aldrich Chem. Co. (USA). The PC was used as received. To purify carotenoids, CAN was dissolved in chloroform and βC was dissolved in

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