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BIOELECTRONIC ASPECT OF ENZYMATIC CATALYSIS

1. INTRODUCTION

Enzymes and their action have been the subject of extensive investigation for a long time. Nevertheless, the full explanation and unified description of the mechanisms underlying enzymatic catalysis as well as a satisfactory reconstruction of the origin and evolution of enzymes are still lacking. Maybe this is caused by too limited knowledge of the phenomena taking place on the submolecular level of the organization of life. It seems that bioelectronics ⟨e.g. 36-37, 39⟩ may give some important insights to fill this gap. A few interesting concepts have been proposed in this regard so far, e.g. the concepts of bioplasma and of the electromagnetic nature of life.

The electronic model of the living system is intimately connected with the above concepts. It ascribes an essential significance of quantum electronic processes to mechanisms that bring about the processes of life. This model is based on the results of the investigation of electronic properties of biological materials (e.g. semiconductivity, pyroelectricity) as well as on the so-called substrate-structure-function (SSF) analogies from typical to solid state physics approach to biomaterials ⟨36 p.169⟩.

The aim of this article is to review some results and concepts which may serve as a basis to formulate a bioelectronic model of enzymatic catalysis. It seems that at least heuristic analogies of the SSF-type between microelectronic and chemotronic devices and enzymatic systems may be of vital importance to this model.

Electronic aspects of enzymatic processes have been a subject of only little investigation ⟨e.g. 7, 22, 35⟩ in the field of the whole enzymology. First of all, the results of quantum-mechanical calculations of the electronic structure of some biomolecules have been taken into consideration, and the significance of the Coulomb-type interactions in processes involving enzymes has been emphasized. Here, however, the elecronic aspects will be understood in a broader sense.

2. THE SUBSTRATE-TYPE ANALOGIES

As far as the analogy of the substrate is concerned, the electronic conductivity of biopolymers ⟨34, 38⟩ is of crucial significance. Such important enzyme as cyto-

chrome oxidase has been proved to have the activation energy of semiconduction as low as 0.26 eV. In connection with this, a semiconduction mechanism of the action of this enzyme has been proposed ⟨11-15, 20⟩. This electronic property is connected with the existence of free electronic charge carriers in biological systems, and with long-range electron transfer in protein structures ⟨21, 31, 42⟩.

The second essential feature of the analogy of the substrate is piezoelectricity of many biological structures, including proteins ⟨e.g. 26-28⟩. With these results, the piezoelectric model of photophosphorylation ⟨8⟩, and the piezoelectric theory of enzymatic catalysis ⟨9⟩, and the quite recently proposed piezoelectric mechanism for the active transport of charge in membranes ⟨32⟩ are coherent.

The high temperature superconductivity of some biostructures ⟨e.g. 19, 29⟩ is another electronic property which has been taken into account. Namely, it has been suggested that it is the superconductivity that may be responsible for the action of enzymes ⟨1-3⟩. Yet, an attempt at experimental detection of high temperature superconductivity in lysozyme was unsuccessful ⟨10⟩. What is more, it has been speculated that relativistic superconductive plasma may exist in some biological structures ⟨16-18⟩ though only recently the syntheses of organic superconductors have been carried out successfully ⟨e.g. 41⟩.

The electret state of many biological materials, including some enzymes, is the fourth property of interest here. The bioelectret behaviour of trypsin, urease, and ribonuclease has been found ⟨33⟩. In connexion with this feature, H. Fröhlich proposed a model in which the action of enzymes was explained on the basis of their electric polarization ⟨23-25⟩. According to this model, the metastabile ferroelectric state in an enzyme system is induced by the interaction of the coherent long-range polarization waves with the field of the elastic strain of the material forming this enzyme. It is proved that enzymes are capable of the storage of the high electric polarization. In Fröhlich's opinion, the adsorption of an ion on a macromolecule may give rise to the local field of the order of 10^6 V/m which may easily induce the electret state in the enzyme. One can even speak about „electric denaturation" of enzymes ⟨33⟩.

3. THE STRUCTURE-TYPE ANALOGIES

As far as the analogy of the structure between a biosystem and, for example, a molecular electronic device (MED) ⟨5⟩ is concerned, it is evident in the structure of sandwich-, and multilayer-types. Various concentrations of free electrons are characteristic of these layers, therefore the p-n type junctions may be formed of them. Surface proteins or the conducting surface layers created by the assemblies of the polar head groups of amphiprotic membrane-forming molecules would form a conductor /insulating barrier/ conductor sandwich similar to such technologically important structures as MIM, MOS ⟨30⟩.

The electronic microenvironment of a given enzyme may differ considerably in dependence on its orientation inside of the membrane or on the surface of it, or in the water phase. If the enzyme is deeply immersed in a lipophilic region of comparatively low permittivity, it has therefore a slight chance to interact with polar mi-

cromolecules, and is surrounded by a relatively stabile microenvironment created by the specific molecular organization of the membrane. On the other hand, if the soluble enzyme is surrounded by the hydrophilic environment of high dielectric constant, various molecules may easily react with its surface groups.

A similar situation may be characteristic of the interior of the macromolecule of an enzyme. For example, the amino acid residues possesing hydrophobic side chains are grouped on the one side of the active center of lysozyme, whereas the residues with the hydrophilic side chains – on the other one. Such a system gives rise to the microenvironments of either low permittivity (hydrophobic residues) or high one (hydrophilic residues). A similar arrangement may be found in the heme center of cytochrome c. Namely, it is surrounded by hydrophilic histidine, on the one side, and by hydrophobic methionine in the other. It may be speculated that the hydrophilic regions may take part in bringing about superconducting states, and the hydrophobic ones – in semiconductivity.

In this context also liquid crystalline structures of biological membranes should be mentioned ⟨e.g. 4⟩. This property is considered to be responsible for the membrane permeability, the adsorption phenomena, and for the catalytic action of biomembrane surfaces.

4. THE FUNCTION-TYPE ANALOGIES

It is of great importance that one of the first molecular electronic devices utilizes enzyme fragments in a hybrid semiconductor-MED detector based on the field effect transistor ⟨6⟩. It appears that finding the functional analogies is more difficult. To make this, one should show which role might be performed by e.g. p-n junctions present in enzymatic systems. In the respect of energetics, these junctions might play a role of detectors or emitters of electromagnetic radiation (e.g. act as electroluminescence diodes), and even of generators of coherent radiation. The putting forward of the analogy of this type is justified by the observation of the resonant influence of nonionizing radiation on some enzymes and of some features of ultraweak luminescence accompanying the oxidative phosphorylation.

5. CONCLUDING REMARKS

Also other types and examples of the analogies of SSF-type may be found, e.g. in the field of chemotronic devices, such as electrokinetic and mechanoelectrical transducers. It seems, therefore, that all the analogies mentioned in the article create a sufficient basis to undertake an attempt at the formulation of the bioelectronic model of enzymatic catalysis.

It is not excluded that various electronic features of enzymes which gave rise to some one-sided hypotheses and theories, as Cope's semiconductor ⟨11-15, 20⟩, Caserta and Cervigni's piezoelectric ⟨9⟩, and the superconductivity hypothesis ⟨1-3⟩ have a common denominator in the existence of the plasma state in biostructures.

Following this line of reasoning, typical of bioelectronic approach to enzymatic catalysis, it has been hypothesized ⟨40⟩ that electron-hole plasma in enzymes and dipole plasma in the water phase may exist, and that the coupling of processes taking place in these plasmas may be responsible for some crucial mechanisms of catalysis.

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BIOELEKTRONICZNY ASPEKT KATALIZY ENZYMATYCZNEJ

Streszczenie

Poznanie mechanizmów działania enzymów jest jednym z kluczowych problemów transdyscyplinarnych. Dużą wartość poznawczą ma badanie procesów przebiegających na submolekularnym poziomie organizacji życia. Problematykę tę podejmuje bioelektronika, która kwantowym procesom elektronicznym przypisuje istotne znaczenie w mechanizmach funkcjonowania różnorodnych zjawisk życiowych.

W niniejszym artykule przedstawiono próbę wskazania możliwości stworzenia bioelektronicznego modelu katalizy enzymatycznej. Postulowano, że u podstaw tego modelu powinny stać heurystyczne analogie substratowo-strukturalno-funkcjonalne pomiędzy układami enzymatycznymi a urządzeniami mikroelektronicznymi i chemotro-

nicznymi. Dokonano przeglądu odpowiednich danych uzasadniających poniekąd istnienie wymienionych analogii heurystycznych w odniesieniu do enzymów. Przy rozpatrywaniu analogii substratu omówiono hipotezy wiążące mechanizmy funkcjonowania enzymów z istnieniem piezoelektryczności, półprzewodnictwa elektronowego bądź nadprzewodnictwa wysokotemperaturowego biostruktur. Rozpatrując analogię struktury zwrócono uwagę na możliwość tworzenia się w układach enzymatycznych elektronicznych złącz typu p-n, warstw sandwiczowych i struktur ciekłokrystalicznych. Wreszcie przy analogii funkcji sugerowano, że złącza p-n w układach enzymatycznych mogą pełnić rolę detektora elektromagnetycznego lub emitera promieniowania spójnego bądź funkcję diody elektroluminescencyjnej. Wspomniano także o hipotezie plazmowego mechanizmu katalizy enzymatycznej. Zgodnie z nią, istnieje plazma elektronowa czy elektronowo-dziurowa w enzymach i plazma dipolowa lub jonowa w elektrolicie przy ich powierzchniach oraz, że sprzężenie zjawisk w tych plazmach może być odpowiedzialne za mechanizm katalizy. Wydaje się, że rozwinięcie tej idei może doprowadzić do głębszego zrozumienia zjawisk życiowych i mieć istotne znaczenie przy rekonstrukcji abiogenezy w aspekcie elektronicznym.

KRYSTYNA SZPANBRUKER

WPŁYW WYBRANYCH PESTYCYDÓW NA WZROST I ROZWÓJ RZĘSY - LEMNA MINOR

Chemiczne środki ochrony roślin, obok doraźnych korzyści z punktu widzenia gospodarki człowieka, stanowią bardzo poważny problem skażenia środowiska przyrodniczego ⟨7, 8⟩. W pierwszej kolejności ulega powolnej zmianie stan fizyczny i skład chemiczny gleby oraz pojawiają się zmiany w składzie ilościowym i jakościowym organizmów glebowych. Środki te nie pozostają tylko w miejscu ich zastosowania. Podlegają one licznym i różnorodnym mechanizmom transportu. Duże ich ilości trafiają do wód śródlądowych stojących i płynących ⟨2, 3, 9, 11, 12, 13⟩: bezpośrednio z terenów poddawanych zabiegom w wyniku zmywania przez wody opadowe i przez znoszenie ich przez wiatr, pośrednio przez wsiąkanie do wód podziemnych ⟨1⟩ i dalej z tymi wodami do stawów, jezior i rzek. Ponadto duża ilość środków ochrony roślin dostaje się do wód powierzchniowych także podczas mycia różnych urządzeń służących do ich rozprowadzania, ze ściekami przemysłowymi i komunalnymi, a także wskutek bezpośredniego stosowania niektórych pestycydów fosforoorganicznych do regulacji składu jakościowego zooplanktonu ⟨4, 6⟩.

W warunkach naturalnych szkodliwe działanie pestycydów, dostających się do zbiornika wodnego jako substancji nieswoistych, polega przede wszystkim na dezorganizacji procesów samoregulacji poprzez hamowanie, obumieranie czy nadmier-