chemical experiments. It is known that in higher plants, 2 such cycles occur, respectively named photosystems I and II, associated through an electron transfer chain, by:

$$P_{700} + P^{*}_{680} \longrightarrow P_{700} + P^{+}_{680}$$

in such a way that it leads to the global endergonic redox reaction:

$$NAD(P)^{+} + H_2O \longrightarrow NAD(P)H + \frac{1}{2} O_2\uparrow + H^{+},$$

$$\Delta G^{\circ\prime} = 52.1 \text{ kcal} \times \text{mole}^{-1} \text{ at pH} = 7$$

and, supplementary to the production of 2 ATP from:

$$ADP + PO_4H_2^{-} \xrightarrow{H_2O} ATP,$$
$$\Delta G^{\circ} \sim +7 \text{ kcal} \times \text{mole}^{-1} \text{ at pH} = 7$$

from 4 photons in the visible range of light frequencies, representing about 200 kcal, which implies an energetic yield of conversion of radiant energy to chemical energy, which is about 30%, i.e., far larger than that obtained from artificial photocells. As shown here, it now clearly appears that the general principles involved in plant photosynthesis do not require for being set in place efficiently all the sophistications which have been produced by evolution, to such an extent that the simulation of photosynthesis in artificial simpler systems would probably be the best way of converting solar energy into electrochemically useful energy in quite an efficient way.

1 All energy balances mentioned have been taken or calculated from the following sources: Handbook of Chemistry and Physics, Ed. R.C. Weast. The Chemical Rubber Co, 1964; Handbook of Biochemistry, Ed. H.A. Sober. The Chemical Rubber Co, 1970; T.E. Barman, Enzyme Handbook. Springer, Berlin 1969; M. Pourbaix, Atlas d'Equilibres Electrochimiques. Gauthier-Villars, Paris 1963.

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Semiconduction theory

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Szent-Györgyi suggested in 1941[1,2] that the application of the concepts of solid-state physics in biology could lead to a better understanding of certain biochemical processes. He proposed the existence of conduction bands in protein structures, producing in 1946 electrical conductivity of dry protein film as the first experimental evidence[3]. In 1949 Evans and Gergely[4] performed a simple molecular orbital calculation and demonstrated theoretically the existence of a banded structure in β-proteins (figure 1) as a consequence of electronic conjugation through the π orbitals of the =C=O ... H–N= hydrogen bridges.

During the following years the suppositions of Szent-Györgyi were confirmed, so that in 1967 Gutmann and Lyons[5] listed 116 biochemicals and organelles exhibiting semiconducting properties that had already been determined. Recently the semiconducting properties of biopolymers were reviewed by Eley[6], Rosenberg and Postow[7,8] and Simionescu et al.[9].

In the present paper, those notions of the semiconduction theory for biomacromolecules are presented (without going into detail) that are generally valid for

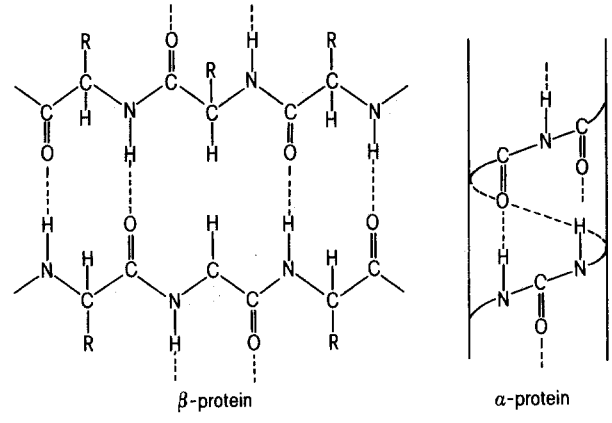

Fig. 1. The hydrogen bridge system in α- and β-proteins.

several biochemical classes, especially for proteins and nucleic acids.

Substances whose electrical conductivity varies as a function of temperature according to the relation:

$$\sigma_{(T)} = \sigma_0 \cdot \exp(-E/2kT) \quad (1)$$

(where E denotes the activation energy for semiconduction, k is the Boltzman constant and T is the temperature in degrees Kelvin) were defined as semiconductors. The electrical conductivity may be of either ionic, electronic or mixed nature. Thus, the conductivity of a given substance may be expressed by the relation:

$$\sigma = [\sum_i z_i n_i \mu_i + \sum_e n_e \mu_e] \cdot e \quad (2)$$

where i is the species of ions present of both signs, with the density n_i, valence z_i and mobility μ_i; e is the species of electronic charge carrier (holes or electrons) with density n_e and mobility μ_e. In the case of mixed conduction, all charge carriers will make their contribution to the total electrical conductivity.

One of the major problems arising when studying electrical properties is the determination of the density and mobility of each charge carrier species in a given substance in order to evaluate its contribution to the total conductivity. The distinction between the electronic (which may take place through either electrons of type n or holes of type p) and ionic (which may take place through atoms or atom groups with + or − charges) conduction can be made by means of solid state electrolysis[8]. Electrolysis will occur only in ionic conduction and may be followed by either the increase in the evolved gas or the decrease of remnant water in a given substance. This phenomenon was studied especially for proteins whose electrical conductivity is very sensitive to hydration. Therefore, if the conductivity is primarly due to ions, the amount of adsorbed water will decrease as a current flows through the sample, because electrolysis will convert some of the water to oxygen and hydrogen. The decreased hydration will manifest itself in a decreasing conductivity as a function of time. When the electrical conductivity does not change in time, the conductivity is electronic (figure 2).

In the case of electronic conductivity, the mobility and sign of each prevailing charge carrier may be determined by the Hall microwave method or the drift method[8]. Determination of the charge carrier mobility is necessary in order to distinguish between the 3 possible models for the charge carrier transport: the band model, the hopping model and the tunnel model (figure 3).

2 energy bands are characteristic for semiconductors: one filled with electrons (the valence band) and the other empty (the conduction band). These 2 bands are separated by a forbidden one. If an electron receives enough energy, it may hop from the valence band to the conduction one, in which it may travel freely. Thus, in an intrinsic semiconductor, the number of electrons in the conduction band must be equal to the holes in the valence band and the activation energy, ΔE, found experimentally, equals the energy difference between the lower filled energy level in the valence band and the upper energy level in the conduction band. For the extrinsic semiconductors, the nature and number of the prevailing charge carriers depend on the electron donating or electron withdrawing nature of the impurity. For the band model, the charge carrier mobility must be higher than 1 $cm^2/V \cdot sec$ and the mobility independent of the temperature. In the case of the other 2 models, the charge carriers are localized in a given place for a

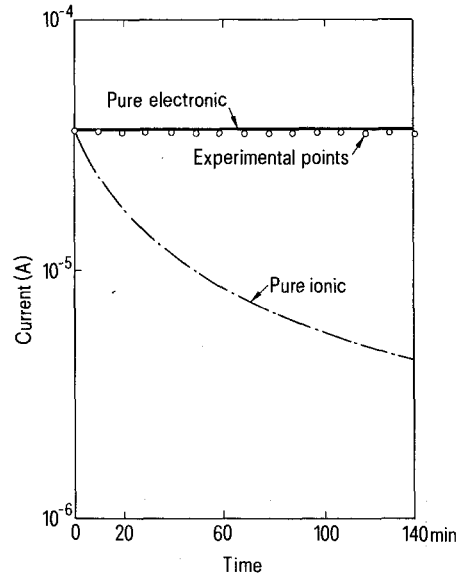

Fig.2. The results of a test of the nature of the charge carriers in haemoglobin with 7.5% adsorbed water. The results indicate that the dominant charge carriers are electronic (either electrons or positive holes) and not ionic at this stage of hydration.

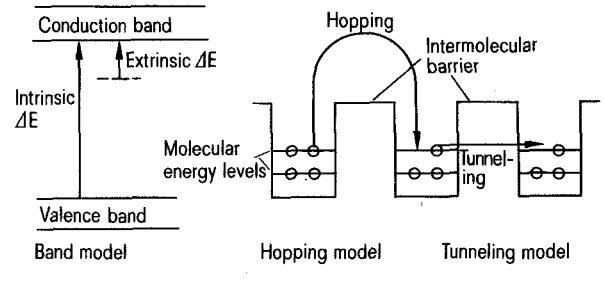

Fig.3. 3 theories of semiconduction. In the band theory, the carriers are excited from either the valence band of the material (intrinsic) or the impurity center (extrinsic) to a conduction band. Conduction may also occur via a hopping of the charge carrier from 1 localized site, over a potential barrier, to a 2nd localized site. The transport between localized sites may, however, occur via quantum mechanical tunneling.

long time and then, in a short time, they may hop over, or tunel through the potential barrier to another place where they will remain for a longer time. For these cases, mobility values lower than 1 $cm^2/V \cdot sec$ are predicted[10].

The main difficulty when studying the electrical properties of biomacromolecules consists of reproducing the conditions of their existence in the living organisms. As is known, biomacromolecules 'in vivo' are not dry and pure, but in a hydrated state impurified by different organic and inorganic substances with small molecules. Apart from the fact that the adsorbed water may act as an impurity, in certain cases the different amount of hydrating water changes the biomacromolecule conformation. This phenomenon is typical for DNA and performs at 75% adsorbed water[11]. For these reasons, the electrical properties of biomacromolecules were first studied in the dry state, the influences of water and small molecule compounds being elucidated afterwards.

Conduction in the dry state

Both synthetic and natural proteins of α- and β-types (figure 1) show in the dry state at 20 °C electrical conductivity and activation energy within the $10^{-17}-10^{-20} \cdot \Omega^{-1} \cdot cm^{-1}$ and 2.3–3.1 eV ranges, respectively. Both DNA and RNA show resistance of the order of $5.10^{-11}\ \Omega \cdot cm^{-1}$ and activation energy of 2.42 eV at 400 °K.

The conduction in proteins, as well as in nucleic acids, is of an electronic nature and represents an intrinsic property of the biomacromolecule. An interesting feature of electrical conductivity in proteins and nucleic acids is the high value of the charge carrier mobilities compared with those in inorganic semiconductors[7]. For instance, the Hall mobilities exhibited by haemoglobin, heated at 90 °C, and DNA are equal to 2 $cm^2/V \cdot sec^{-1}$ and 10–15 $cm^2/V \cdot sec^{-1}$, respectively[9].

The semiconduction model in α- and β-proteins

The simplest biopolymer protein was selected to exemplify the conduction model in biopolymers. In 1960 Eley and Spivey[12] proposed a model for conduction in α- and β-proteins. They assumed the band model for describing the electron mobility through the CO:HN system of molecules with α- or β-structure and proposed a mechanism of tunneling the potential energy barrier located at the chain end of the unit given in figure 4. The system $(=C=O\ldots H-N=)_n/d$ is supposed to be continuous over a distance $l=n \cdot d$, where d is the unit length. Thus, in α-proteins l is the α-helix length, whereas in β-proteins it is related to the discontinuity in the coplanar polypeptide chains. At the end of each unit-chain a potential barrier is presumed, probably associated with a surface trap. Thus, an electron excited thermally above the energy gap, ΔE, tunnels through the potential barrier, of width 'a', similar to the hole remaining in the valence band. Tunneling through the potential barrier between the adjacent CO...HN groups is the difficult step.

Conduction in the hydrated state

Water adsorption by both proteins and nucleic acids results in a marked increase in electrical conductivity and a decrease in the activation energy. Over a wide hydration range, the electrical conductivity varies according to the relation:

$$\sigma(m) = \sigma_D \exp(a\, m) \qquad (3)$$

where $\sigma(m)$ denotes the electrical conductivity in the hydrated state, σ_D is the dry state conductivity, m is the percentage of adsorbed water and a its a constant. In the case of haemoglobin (figure 5), the water adsorption causes a conductivity increase by 8 orders of magnitude and an activation energy decrease from 2.4 to 1.1 eV, whereas in the case of the nucleic acids, a conductivity increase by 9 orders of magnitude results. Furthermore, whereas for a small amount of adsorbed water the conductivity is elec-

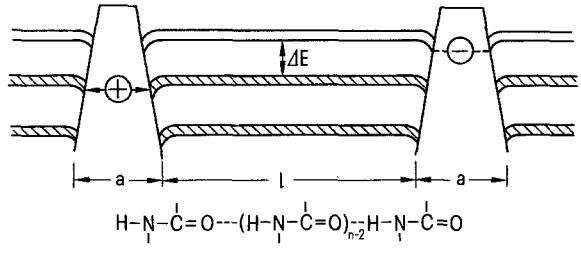

Fig. 4. The model for protein semiconduction.

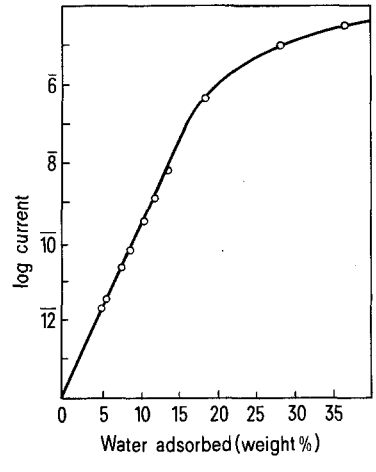

Fig. 5. Conductivity of a haemoglobin tablet as a function of the water adsorbed at a constant temperature (T = 298 °K) and constant applied voltage. Up to about a value of 18%, the current increases exponentially with increasing water adsorption. Above this value it approaches saturation.

tronic, at a certain hydration level, corresponding to 3–4 V_m (Brauner-Emmett-Teller monolayer volume) for most proteins, ionic conduction appears. At this hydration level, the water is not completely localized and begins to form a continuous water layer with numerous hydrogen bonds. The conduction may partially, proceed through this water layer.

At present there are 2 mechanisms explaining the change of electrical properties by hydration.

Postow and Rosenberg[13] have advanced an intrinsic mechanism for the hydrated state conduction. They supposed the conductivity increase to be due to an increase in the protein dielectric constant resulting in a lowering of the energy necessary for separation of the charges, and stabilization of the charge carriers (electrons and holes) so that their number will increase.

Eley and Leslie[14] have proposed an impurity mechanism according to which the water molecules are adsorbed on the polar groups, the C=O...H–N hydrogen bonds being included, leading to the so-called charge transfer adsorbed state where water acts as a donor impurity.

Although both theories might be criticized[9], the similar effects of water on different biomacromolecules, as shown above, are indicative of a similarity between the conduction mechanisms of different biochemicals.

Influence of other small molecules on the electrical properties

Equation 3 was demonstrated to be valid also for other small molecules, such as methylic alcohol, formic acid, different esters etc.[8].

The protein interactions with both prosthetic groups and electron acceptors increase the electrical conductivity and decrease the activation energy. For instance, by extracting ferrous protoporphyrin from haemoglobin, the electrical conductivity decreases by 1 order of magnitude[15]. The chloranil forms complexes with bovine plasma albumin, whose conductivity increases by 6 orders of magnitude, compared with those of albumin, and activation energy decreases from 2.86 to 1.06 eV[16]. The bovine plasma albumin may form binary, ternary and quaternary charge transfer complexes with β-carotenes, chlorophyll and β-methyl naphthoquinone. Activation energy and resistivity change from the 2.86 eV and $5.10^{17}\ \Omega \cdot \mathrm{cm}^{-1}$ values for albumin to 2.51 eV and $5.10\ \Omega \cdot \mathrm{cm}^{-1}$ for complexes, respectively[17].

An interesting behavior has been demonstrated by Eley[18] for electron mobility in mitochondria. Thus, very small amounts of potassium cyanide (10^{-4} M) diminish the initial mobility value to one-third, while antimycin-A and rotenone in high concentrations do not significantly modify the mobility.

Conclusions

The semiconducting properties of biomacromolecules are a certainty which cannot be neglected when models are proposed for explaining some biological function such as, enzymatic activity of cytochrome oxidase, olfactory transduction, visual reception, properties of the cellular membranes, etc.[6,7,9]. Although a perfect correlation does not yet exist between the results of molecular orbital calculations and experimental data regarding the electrical conduction in proteins and nucleic acids[9], a profound study on the aspects connected with intrinsic mechanisms of conduction in biomacromolecules, as well as on dependence of electrical properties on the impurities acting in vivo, should increase our understanding of biophysical phenomena.

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