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Enzyme Systems and Their Logic

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Editorial

The concept of system embodies different aspects that are all important in trying to understand the logic of biological events. This is precisely the case of enzyme reactions that can be studied in details *in vitro* even though the knowledge of enzyme kinetics offers little information about the way the enzyme work *in vivo*. As a matter of fact, for a number of reasons that will be considered below, enzyme reactions may be quite different when considered *in vitro* and *in vivo*. For reasons that will appear later, an enzyme reaction is an element of a system and, for that reason, should be considered in a different perspective. Within the living cells, enzymes interact with different cell components in such a way they constitute systems with properties far more subtle and complex than the intrinsic enzyme properties. The aim of this short communication is to discuss briefly some properties of these *enzyme systems*.

Compartmentalization of enzyme reactions within a living cell can possibly give birth to a system that possesses properties that are novel relative to the properties of the same enzyme considered in isolation. In such a system, for instance, enzyme reactions that are thermodynamically disfavored can perfectly occur. This can be due, for instance, to the fact that some enzyme reactions are coupled with the vectorial processes of ligand transport across membranes. ATP synthesis in mitochondria and chloroplasts is perhaps the most obvious example of this type of process. Moreover the fact that some enzyme reactions are coupled with transport processes across membranes explains the occurrence of events that are thermodynamically disfavored. In such events enzymes involved are *part of a system.*

In stirred dilute solutions, diffusion of molecules is a fast process relative to enzyme activity and under these conditions the *system* is solely dependent upon the intrinsic enzyme activity. If, however, the diffusion rate is lowered, as it occurs within the living cells, the situation is completely changed for the rate of the process is not that of enzyme catalysis alone but that of a system resulting from the coupling of ligand diffusion and enzyme reaction. A novel property that could appear under these conditions is the possible existence of *hysteresis*. This means that depending on the bulk external concentration is increased, or decreased, the corresponding *local* substrate concentration within the membrane will be different. In other words, the system is able to sense whether a given fixed substrate concentration is reached after an increase, or a decrease, of a previous concentration. The bound enzyme system is then the physical model of a *biosensor*.

If an enzyme is embedded in a membrane the effects of electrostatic repulsion or attraction of a charged substrate mimics some kind of cooperativity. Moreover the response of the bound enzyme to subtle changes of substrate concentration becomes sensitive to slight changes of ionic strength even if the enzyme is *per se* insensitive to these variations. In such a situation, and contrary to a common belief, biological networks are not controlled by "allosteric enzymes" but by a set of enzymes belonging to the same pathway. Owing to this *molecular democracy*, many enzymes of the same pathway may be involved in the control of this network.

An open metabolic cycle may display sustained oscillations if at least one of the enzymes involved in the pathway displays nonlinear terms. The simplest event to be expected is the one where an enzyme is inhibited by an excess substrate. If the corresponding cycle is taking place at the surface of a charged membrane, electric repulsion effects exerted by this membrane may generate oscillatory dynamics even if the enzyme rate laws do not involve nonlinear terms. Such systems have been termed "dissipative structure" by Prigogine.

An even more subtle degree of complexity can occur when two, or more than two, enzymes that catalyze different reactions are associated to form an enzyme complex. Under these conditions, the association of different enzymes results in alterations of the behavior of the individual enzymes that form the complex.

It seems that any non-vitalist biological theory relies upon either of the preconceived ideas: the belief that the macroscopic properties of living systems relies upon a detailed knowledge of the structure of "informational macromolecules" such as DNA and proteins; the attempt to apply equilibrium thermodynamics to "living entities"; last but not least to consider there exists *biological systems* that possess properties and functions distinct from those that characterize the elements of these systems. Modern experimental and theoretical studies have clearly shown that the properties of an enzyme-catalyzed chemical reaction involved in a system may be completely changed depending on the nature and properties of the system itself. It is important to stress again that the concept of system can be approached through a rigorous physico-chemical study and is neither vague nor imprecise. There is no doubt, for instance, that the so-called "oscillatory enzymes" are in fact *systems* that associate enzymes, which do not display any periodic behavior, with other molecular elements. It is the system thus formed that possesses periodic properties.