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## II. MOLECULAR DIPOLES AND CHIRALS

### A. ELECTRIC DIPOLE MOMENTS

Dipolar electric moments and dielectric polarization have been surveyed by Errera (1928, 1935). Further study of the dielectric response of matter to an applied electric field has contributed to the measurement of molecular dipole moments (Price, 1969). The induced dipole moment per unit volume or polarization consists of two components: a *polarizability* one which arises from the distortion of the electronic distribution of the substance, and an *orientation* component. Farley and McClelland (1990) have demonstrated that even in collisionless molecules, "hot isolated polyatomic molecules can reorient in response to an external field, thereby giving rise to this second component of polarization".

### B. MINERAL DIPOLES

#### 1) *Dipolar water*

Among recent and complementary knowledge about water biophysics and relevant to polarity, mention can be made of Saenger's 1987 review. It mainly concerns the relationships between hydration water and hydrogen bonds. Hydrogen bonding dynamics involves flip-flops and movement of water along the surface of macromolecules. Water would not have its particular properties if the molecules were not associated by hydrogen bonds  $O-H \cdots O$ . If the O-H group is involved in hydrogen bonding it becomes polarized (see II in I). In the association of water molecules to the surface of proteins or nucleic acids, hydrogen bonding of type (water)  $O-H \cdots Y$  is the main attractive force. When the  $O-H \cdots O$  bonds all run in the same direction, this is called *homodromic*; it is indicative of the influence of the cooperative effect. When a water molecule donates two hydrogen bonds this gives rise to *heterodromic* situation, where hydrogen bonds are randomly oriented.

According to the idealized structural model for water presented by Finney (1982), the simplest picture of the molecule "assigns partial charges to the two hydrogens and the two lone pairs which are considered to be disposed in an approximately tetrahedral manner. Each molecule is capable of forming four hydrogen bonds to neighbouring molecules" (see also I). Among the three proposed models of the water-water hydrogen bond, the PE model (water molecule electron distribution in terms of an electrical multipole expansion, see Barnes *et al.*, 1979) represents the water molecule electron distribution in an electrical multipole expansion. According

to Finney (1982), "the experimental dipole moment and quantum mechanical quadrupole are used, together with a dipole polarizability to try to handle the cooperative effects". Switching on polarizability in the PE model would therefore affect only the dipole-dipole and dipole-quadrupole energy terms (Finney, 1982).

The local dipolar field of protons of liquid water is averaged out by fast isotropic rotation and translational diffusion, and this gives a single narrow line in the NMR spectrum. In a molecular or biological system which can restrict water motion, causing an anisotropic averaged orientation, the NMR spectrum of the preferentially oriented water molecules can be given by a line pair or doublet. Lenk *et al.* (1980) have reported such NMR doublets spectra due to "structured" water in plant systems.

A typical example of efficient proton translocation across or along the surface membrane is the movement of protons across a cell membrane after their generation in some oxidation process. A high level of proton conductivity is extremely rare in crystalline solids. Thomas and Farrington (1982) have proposed that the proton conduction mechanism in one of the very best crystalline proton conductors so far studied ammonium/hydronium  $\beta''$ -alumina is a useful model mechanism for biological proton transfer. This proton conduction mechanism deduced from an accurate single crystal neutron diffraction study involves a classical Grotthus-type mechanism (see below).

In relationship with bilayer membranes (see IV.B.2) it should be pointed out that "an ion in water is stabilized by the favorable interactions of the water dipoles, the hydration energy. To remove an ion from water and place it in the middle of a membrane is unfavorable because of the loss of this hydration energy". The most successful model for quantifying this is the Born model described in Gennis (1989). In addition to this Born energy, a second component due to the polarization arises at the dielectric interface. An "image energy" results from the "presence of a charge on one side of the interface which causes the dipoles in the medium on the other side to reorient".

Cell water is modified by solvation which arises when water abuts a cell surface. Molecules become restricted in their motions and a greater proportion of them have four (rather than three or fewer) hydrogen bonds with their neighbours. Water modified in this manner is called vicinal (see I and Drost-Hansen and Singleton (1989).

Virtually all of the water in cells is considered to exist as polarized multilayers arising from fixed charges on extended protein surfaces. Cardinal sites exist on these particular proteins, the degree of binding for a given ion being influenced by a number of factors. Clegg (1982) further commented "ATP binding at the cardinal site leads to cooperative alterations and the selective accumulation of  $K^+$  over  $Na^+$ , and generates the polarized multilayers of water; ATP splitting and the removal of ADP results in a movement of the system to a lower energy state in which the ion selectivity is lost as is the polarization of water".

Protons can be transferred along lipid/water interface in the absorbed water molecule network by a Grotthus-type mechanism (ref. in Tocanne and Teissié, 1990, see also IV.B.2.a).

## C. ORGANIC DIPOLES

### 2) *Multiple molecules (polar chains)*

Charge transfer molecular interactions are of high significance in biology (Sklifkin, 1980). Electrons are delocalized in molecular conjugated systems (alternate single and double bonds). The polarization of these molecules is enhanced when they carry hydroxy-substituent(s) which behave as electron-attracting groups. Consequently, Pont and Pezet (1990) could suggest that “the polar interaction of these molecules with membranous proteins could lead to a destruction of the cellular membranes by depolarization” (see IV.B.2.d). This could account for the biocidal effects of highly conjugated phenol derivatives such as the natural hydroxystilbenes which are efficient protectors of grape berries against the grey mold *Botrytis* (Pont and Pezet, 1990).

## D. CHIRAL MOLECULES

Pasteur (1884, see I) audaciously extrapolated from molecular asymmetry the famous aphorism “la vie est apparue dans une brisure de symétrie”. If we equate asymmetry and polarity, this would therefore mean that polarity is basic to the arisal of living matter.

From atoms to human beings, nature is asymmetric with respect to chirality (Gardner, 1979) and “clues are beginning to emerge that connect chirality on different levels”. Thus, and as resulting from the weak nuclear Z force between electrons and nuclei, all atoms are also chiral. Consequently, the interaction that causes the helical motion does not conserve parity, and the mirror-image atom with a right-handed helical electron flow does not exist in nature (Hegstrom and Kondepudi, 1990, see I.B).

Chirality has its fundaments in the asymmetry between electron and positron; this asymmetry follows up in the hydrogen atom and reaches its full expression in the carbon asymmetry (see II.D). The basic molecules of life all have a specific handedness. They are therefore asymmetric (see I.B): its amino acids are left-handed, whereas its sugars are right-handed (see I). Chiral compounds which dissociate into enantiomers display a sharp difference in biologic activity. Chemists have been able

to induce a selection between two enantiomers and to develop methodologies for asymmetric syntheses initiated from prochiral center (Mosher, 1971, in Morrison, 1983-1985; see Oppolzer, 1987 and Holmstedt *et al.*, 1989). Chiral auxiliaries have been produced around asymmetric centers using organo-copper reagents. New bondings have thus been obtained with the concourse of highly stereo reactions in compounds such as diverse drugs ( $R(+)$ - $S(-)$  thalidomide, etc.), pheromones, and perfumes (Oppolzer, 1987).