

These results may be explained on lines well known for inorganic semiconductors. The chloranil molecules are taken to accept electrons from the protein, creating positive holes in its conductivity band⁸. On the other hand, water is an electron donor, and by neutralizing positive holes lowers the conductivity of the bovine plasma albumin-chloranil complex. Ammonia gas shows a similar electron-donor behaviour to water, as would be expected. The twelve-fold increase in resistivity is consistent with a filling up of the positive holes (10⁸ increase) followed by a donating of electrons into the conductivity band (10⁵ decrease). It seems probable, therefore, that in the living cell proteins may show *N* (negative) or *P* (positive) behaviour, depending on their environment, whether aqueous or lipoidal, presence of electron acceptors, free radical sources, etc. It is possible that further work will show that such changes in conductivity may result in steady-state values sufficiently high to be significant for models of electron-transport¹, carcinogenesis⁹ and other phenomena in the living cell.

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Semiconductivity in Hydrated Haemoglobin

HÆMOGLOBIN is regarded as a model for a large class of oxidation enzymes, where electron mobility may be of biological significance¹⁰. In the dry state its very low specific conductivity, about 10⁻¹⁸ Ω⁻¹ cm.⁻¹ at 30° C., is attributed to electron and hole mobility¹ in the CO . . . HN bridge system⁸. Water is adsorbed on natural, or methanol-denatured, haemoglobin, corresponding to a Brunauer-Emmett-Teller 'BET monolayer volume' *V_m* of 319 moles/10⁵ gm. protein, whereas a close-packed monolayer of water molecules over all the molecular surfaces throughout the crystal would involve 1,160 moles/10⁵ gm. protein¹¹. The molecular dimensions for the latter calculation are taken from X-ray data¹² which also show that water molecules do not penetrate within the actual molecules, but only over the molecular surfaces. We have studied the effect of adsorbed water on the semiconductivity of a solid specimen of methanol-denatured haemoglobin, allowing three days for equilibrium for each point. The result in Fig. 1 shows that there is a large increase in conductivity which reaches a constant value at about *V_m*. Thereafter, there is little change until a relative vapour pressure of about 0.9, corresponding to 4*V_m*, when the conductivity increases sharply to about 10⁻⁸ Ω⁻¹ cm.⁻¹ at 30° C.

Following the result of the previous communication it, is suggested that initially water molecules are held on special sites and donate electrons into the conductivity band of the protein molecule giving an 'N-type (negative) protein', where a high mobility is expected throughout the crystal⁸. To accord with earlier suggestions¹³, and the increase in conductivity, these sites may be CONH groups adjacent to polar side chains. This view differs from that of Baxter¹⁴, who suggested that electrons tunneled from one adsorbed water molecule to the next. As the physical surface becomes filled up around 4*V_m*, we expect proton conduction to set in within the monolayer of adsorbed water, along lines suggested by Riehl¹⁵. Proton conduction, with 10⁻⁹ Ω⁻¹ cm.⁻¹, has been

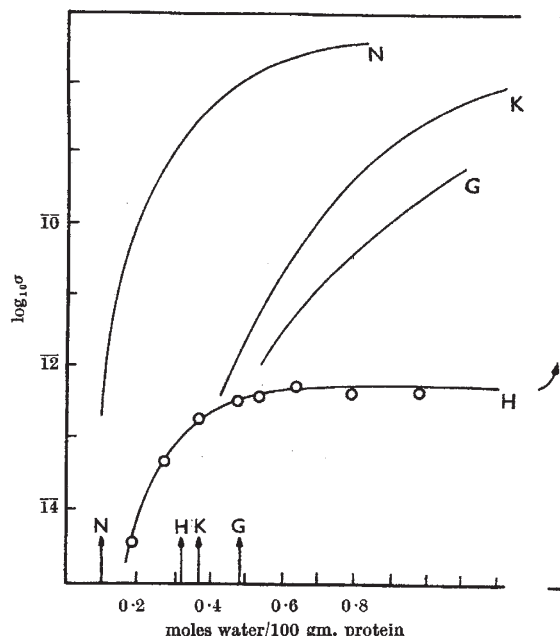


Fig. 1. Specific conductivity σ , Ω⁻¹ cm.⁻¹ as a function of adsorbed water for nylon at 25° C. (*N*) (ref. 9), keratin at 25° C. (*K*) (ref. 9), gelatin at 32° C. (*G*) (ref. 11) and haemoglobin (*H*) at 30° C. The arrows mark the values of the Brunauer-Emmett-Teller monolayer adsorption (refs. 11 and 17)

demonstrated for keratin with 15 per cent water¹⁶, about 2.5*V_m*¹⁷ (see Fig. 1). Similar 'high' specific conductivities may be calculated for gelatine with 2.5*V_m* adsorbed water¹⁸. It may be that the relatively marked effect of water on the conductivity of these two fibrous proteins, and its even more marked effect on nylon^{16,19} point to the operation of yet a third effect due to adsorbed water on flexible chain molecules containing CONH groups, that is, the plasticizing effect of water molecules on chain movement, facilitating transfer of protons between NH and CO groups in different chains, first described by Baker and Yager¹⁹.

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