Infrared Absorption Spectrum of Water adsorbed on α-Helical Synthetic Polypeptides

I REPORT here some observations on the polarized infrared absorption spectrum of water adsorbed on orientated synthetic polypeptide films. The results suggest that the water molecules are adsorbed at specific sites and orientations with respect to the substrate molecules.

Orientated films of high molecular weight synthetic polypeptides in the α-helical conformation were prepared by collapsing to one end of a Langmuir trough monolayers spread on the water surface. The method used to spread the monolayers and to remove the collapsed film has been described previously[1,2]. Sufficient monolayers were spread to give a specimen with an absorbance of 1·5 or greater for the amide I band. Films were mounted on barium fluoride plates and dried to a predetermined humidity. Where necessary, scatter of radiation from the surface of the specimen was reduced by allowing a drop of chloroform or benzene to flow across the surface so that it softened and became compacted. This treatment improved the quality of the spectra and probably modified the crystallinity of the specimen, but was not essential to see the main features described. Because the OH-stretching band lies close to the amide A (NH-stretching) band, it is helpful (but not essential) to reduce the NH absorption by using N-deuterated polymer and spreading the monolayers on 0·01 M HCl on which the back exchange of deuterium is slow[1].

High molecular weight specimens of poly-D-alanine, poly-γ-ethyl-L-glutamate and poly-γ-methyl-L-glutamate have been examined with particular reference to the 2,000–4,000 cm⁻¹ spectral range. Although the strength and shape of the water absorption band varies from one polymer to another, three main features are common to all the polymers: (1) the OH absorption is not centred about 3,400 cm⁻¹ as in liquid water, but is displaced to around 3,500 cm⁻¹; (2) the band is clearly made of two or three components; (3) overall, the band exhibits marked perpendicular dichroism. Fig. 1 illustrates these features for poly-γ-methyl-L-glutamate, together with the NH and N²H stretching bands (about 3,300 and 2,450 cm⁻¹), which
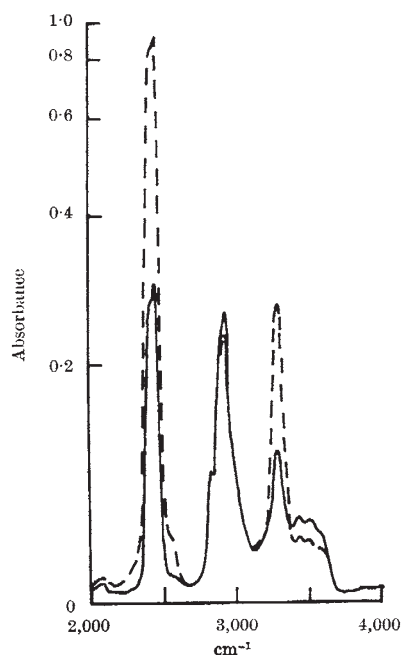
are of opposite dichroic character to the water band, and the CH bands. The water band has components at about 3,440, 3,510 cm⁻¹ and 3,570 cm⁻¹. Poly-γ-ethyl-L-glutamate has three similar bands and poly-D-alanine has a band at about 3,470 cm⁻¹ with a shoulder at 3,530 cm⁻¹.

Because the frequency of the water absorption band is roughly mid-way between that of the free and hydrogen-bonded OH stretching frequencies it is probable that the hydrogen bonding component of the binding is weak. The dichroism and splitting of the band into two or three components is good evidence that the molecules are in specific orientations and sites with respect to the polymer. If the band is attributed mainly to the OH antisymmetrical stretching vibration (normally the strongest), which has a transition moment parallel to the line drawn through the hydrogen atoms, the molecules are orientated on average with this direction fairly close to planes drawn perpendicular to the helix axis. An estimate of the angle can be made by using the direction of the NH and N²H transition moments to give a measure of the orientation of the polymer. The usual model for fibre orientation is assumed with a fraction of perfectly orientated polymer and the rest disorientated[3], and the water is taken to be distributed in proportion over both fractions. This leads to the H–H direction being within about 25° to the plane perpendicular to the axis of the helix.

Weak perpendicular dichroism of the same water band has been observed in hydrated α-keratin by Bendit[4], who found the frequency to be 30–40 cm⁻¹ higher than in liquid water. Although the spectrum was very similar to that of an equivalent thickness of liquid water, it is probable that the observations are closely related to the present work.

A tentative explanation of these observations, consistent with the views of Bendit for keratin, is that the water molecules orientate with a hydrogen atom directed towards the peptide oxygen, possibly forming a weak hydrogen bond to it, with the H–H direction of the water molecule within 25° to the plane perpendicular to the helix axis. In this situation it is probable that the water dipole will interact strongly with the peptide dipole. This orientation would account for the positive sign of the surface potential when a monolayer of α-helices is spread on water[1], if on a clean water surface the hydrogen atoms are normally directed downwards[5]. In the case of the glutamate polymers an additional interaction may occur between the water and the side chain carbonyl.

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Involvement of Articular Cartilage in a Linear Relaxation Process during Walking

A KNEE joint consists essentially of a pair of articulating bone surfaces lined with cartilage; the latter is swollen with an aqueous solution of protein and salts and contained within a sac (synovial membrane). The solution to prob-