The Adsorption of Water Vapor and Other Gases by Proteins

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For many years investigators have been interested in the amount of water held by protein molecules, and many studies have been made of the hydration of proteins. These studies have, however, led to little contribution to the fundamental questions of protein structure. I believe that the measurement of the amount of water vapor held by proteins at different values of the partial pressure of water, and of the amount of other gases similarly adsorbed by proteins may be an extremely useful method of obtaining information about the structure of proteins. Interesting experimental data on the hydration of proteins held in atmospheres of varying relative humidity have been reported in the September issue of the Journal of the American Chemical Society by Henry Dull and in the September issue of the Journal of Chemical Physics by T. M. Shaw. These authors interpreted their data by the application of the Brunauer-Emmett-Teller theory of multi-layer adsorption, obtaining in this way a value for each protein of the surface area on which water vapor may be adsorbed. These effective surface areas were found to vary between ten percent and forty percent of the total surface area of the proteins when spread in thin films. No very significant interpretation of the values of the surface areas was made.

It occurred to me that a comparison of the number of water molecules held by primary adsorption and the number of amino acid residues of a polar nature, that is, capable of forming hydrogen bonds with the water molecules, might be interesting. This has indeed been found to be so.

The number of water molecules held strongly by silk, as given by the interpretation of Bull's data, is just equal to the sum of the numbers of serine and tyrosine residues, these being the only polar residues in the protein. For other proteins there is similar evidence that primary attraction for water vapor results in the attachment of one molecule of water to each polar residue.

A very interesting conclusion may be made from the data for gelatin. It is found that the number of water molecules held strongly by gelatin is equal to the total number of amino acid residues normally considered to be polar, plus the number of proline residues. In most proteins the imino and carbonyl groups of the peptide links seem not to have very strong attraction for water. The result for gelatin suggests that the proline residue does attract a water molecule, presumably because the bond between the hydrocarbon side chain and the nitrogen atom liberates a carbonyl group, which otherwise would be used in hydrogen bond formation with an N-H group of a peptide bond, and the liberated carbonyl attracts and holds a water molecule.

The protein salmin shows a unique behavior in its attraction for water. The adsorption isotherm may be interpreted by a theory which represents an extension of the Brunauer-Emmett-Teller theory. When this interpretation is made it is found that the first process is the addition of one water molecule for every two arginine residues, this molecule presumably being bonded to both residues by means of its two hydrogen atoms. The next step consists in the addition of an equal amount of water, presumably resulting in a situation in which each arginine residue holds one water molecule. Then there are introduced successive layers of water molecules, the amount of water in each layer being just the amount necessary to produce a unimolecular layer between layers

of the protein of the thickness present in monomolecular films; the amount of water in each of these layers if 3.2 x that held by the primary process.

I think that it is very probable that similarly detailed information can be obtained about other proteins with use of experimental data on the adsorption of water. It is not unlikely that careful measurements made at very low relative humidities would indicate the addition of water successively to the groups with diminishing attraction for the water molecules, perhaps permitting an amino acid analysis of a protein to be made by this technique. The study of other gases, such as ammonia, hydrazine, hydroxylamine, hydrogen peroxide, and hydrogen sulfide, might provide additional valuable information. It is clear that the job of collecting experimental data would be a large one, but that the results presumably would justify it.