# THE SORPTION OF WATER VAPOUR BY YEAST CELL WALL AND OTHER POLYSACCHARIDES

by

D. H. NORTHCOTE

*Biochemical Laboratory, University of Cambridge (England)*

## INTRODUCTION

Investigations of the water vapour sorption isothermals of cotton and starches have indicated that these studies may give information into the internal association or hydrogen bonding which occur between the hydroxyl groups of the polysaccharides. An extensive survey of the sorption of water by various proteins has been made by BULL[1]; these data and those of a similar nature including those of URQUHART AND WILLIAMS[2] for cotton have been used by HAILWOOD AND HORROBIN[3] to test an isotherm developed by postulating that the sorption of water depends on simple solution and on the formation of a hydrate with a definite unit of the polymer. The fraction of units in a polymer accessible to the water molecules can be calculated from the isotherm, and in the case of cotton the "crystalline to amorphous ratio" so obtained is of the same order as that derived from the X-ray evidence.

The mechanism whereby water is associated with a polysaccharide is important not only for the information it gives concerning the internal structure of the polysaccharide but for storage compounds such as glycogen and starch it is relevant to any discussion of the osmoregulation of the cell. The permeability of a structure such as a plant cell wall must also be considerably influenced by the manner in which the water molecules are associated with the polysaccharides of which the wall is composed.

Accordingly sorption isotherms have been studied of the polysaccharides of the yeast cell wall (NORTHCOTE AND HORNE[4]); glycogen and other compounds in which the biological functions were fairly well known. The chemical structures of these polysaccharides had already been investigated in some detail, and this has permitted a more systematic comparison of the sorption with molecular structure than had been possible hitherto. In addition the data have been used to test the isotherm of HAILWOOD AND HORROBIN[3] when reasonable agreement was obtained between the calculated and observed sorption values. The theory on which the development of the isotherm was made has been used to indicate the type of interaction between the water and polysaccharide molecules.

## METHODS AND MATERIALS

*Materials.* The methods of preparation and the characteristics of the polysaccharides were those described by the authors listed below.

*References p. 479.*

a. Glycogens.

| | |
|---|---|
| i. Yeast. | Prepared by the cytolysis of the cell with 3% NaOH and extraction of the polysaccharide by dilute acetic acid. NORTHCOTE[5]. |
| ii. Rabbit-liver. | BELL[6]; BELL AND MANNERS[7]. |
| iii. Mytilus edulis. | BELL[8]; BELL AND MANNERS[7]. |
| iv. Helix pomatia. | BELL AND MANNERS[7]; BALDWIN AND BELL[9]. |

Samples of glycogens ii, iii and iv were kindly given by Dr D. J. BELL.

| | |
|---|---|
| b. Yeast glucan. | BELL AND NORTHCOTE[10]. |
| c. Acetylated yeast glucan. | BELL AND NORTHCOTE[10]. |
| d. Yeast Mannan. | HAWORTH, HIRST AND ISHERWOOD[11]; HAWORTH, HEATH AND PEAT[12]. |
| e. Acetylated yeast mannan. | HAWORTH *et al*[11]. |
| f. Dextran. | Leuconostoc mesenteroides. Fractionated according to INGELMAN AND HALLING[13]. Mol. wt. 150,000. This material was kindly given by Dr L. E. MARTIN of Benger's Ltd. |

*Data for the sorption isothermals.* The materials were dried to constant weight at 100° and 0.01 mm Hg over $P_2O_5$ for 6 h, cooled *in vacuo* and approx. 0.5 g transferred to a well stoppered, tared weighing bottle and weighed. The bottles were placed in jars containing, in a separate compartment, approx. 200 ml of a soln. of $H_2SO_4$ of known strength (WILSON[14]). The jars were kept at constant temp. (± 0.5°) and series of experiments were carried out at 26° and 45°. The weighing bottles were opened and the jars sealed by a close fitting plastic cap which came flush with the top of the jar on a soft cardboard ring. To ensure that the jars were air tight cellulose tape was bound around the outside of the cap of the glass jar. After approx. 144 h the stoppers were replaced in the weighing bottles which were removed and weighed. The bottles were returned to the jars for a further 48 h and then reweighed. This process was continued to constant weight (± 0.2 mg). Usually 168 h were sufficient for equilibrium.

The desorption isothermals were obtained in a like manner except that the samples were first equilibrated at a relative humidity of 91 % and then transferred to jars at the lower relative humidity.

## RESULTS

*Sorption isothermals.* The usual sigmoid shape of the sorption isothermals at 26° and 45° was observed for all the polysaccharides. The results are shown in Tables I and II.

*Application of the isotherm of* HAILWOOD AND HORROBIN[3].

$$\frac{Mr}{1800} = \frac{ah}{1 - ah} + \frac{a\beta h}{1 + a\beta h}$$

where $M$, $a$ and $\beta$ are constants, $h$ is the relative humidity (%) and $r$ is the % regain (the total g of $H_2O$ sorbed/100 g dry polysaccharide). Since the mechanism of uptake

TABLE I

REGAIN VALUES

*C*, calculated after sorption. *S*, observed after sorption

| *h* % | *Yeast glucan* | | | *Rabbit-liver glycogen* | | | *Yeast glycogen* | | | *Mytilus glycogen* | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | *C* | *S* | *D* | *C* | *S* | *D* | *C* | *S* | *D* | *C* | *S* |
| 5 | 3.5 | 3.6 | 5.1 | 3.2 | 3.2 | 3.5 | 2.8 | 2.5 | 4.0 | 2.5 | 2.5 |
| 11.5 | 6.1 | 6.0 | 8.9 | 5.4 | 5.2 | 6.0 | 5.0 | 5.5 | 6.4 | 4.9 | 5.0 |
| 17 | 7.7 | 7.6 | 10.3 | 6.6 | 6.8 | 8.0 | 6.3 | 6.8 | 7.9 | 6.3 | 6.5 |
| 31 | 10.8 | 10.8 | 13.3 | 9.0 | 8.9 | 10.5 | 8.8 | 8.6 | 10.7 | 8.9 | 8.9 |
| 38.5 | 12.3 | 12.5 | 14.4 | 10.1 | 10.0 | 12.0 | 9.9 | 9.7 | 12.2 | 10.1 | 10.1 |
| 57 | 16.3 | 15.9 | 17.5 | 13.3 | 13.2 | 15.2 | 12.8 | 12.9 | 15.6 | 12.9 | 13.1 |
| 68 | 19.2 | 17.9 | 19.4 | 15.7 | 15.3 | 17.2 | 14.6 | 14.9 | 17.4 | 14.8 | 14.8 |
| 77 | 22.4 | 20.0 | 21.6 | 18.3 | 17.7 | 19.1 | 16.3 | 17.9 | 19.1 | 16.3 | 17.1 |
| 82.8 | 24.9 | 23.6 | 24.3 | 20.4 | 20.2 | 20.2 | 17.6 | 20.2 | 20.0 | 19.6 | 18.8 |

*References p. 479.*

TABLE II

REGAIN VALUES OF $r$ (%) AT 45°

$C$, calculated after sorption. $S$, observed after sorption. $h$, relative humidity.

| $h$ % | *Yeast glucan* | | *Rabbit liver glycogen* | | *Leuconostoc dextran* | | *Acetylated yeast glucan* |
|---|---|---|---|---|---|---|---|
| | $C$ | $S$ | $C$ | $S$ | $C$ | $S$ | $C$ |
| 7 | 4.2 | 4.1 | 3.1 | 2.9 | 3.1 | 2.9 | 0.5 |
| 14 | 6.7 | 7.0 | 5.2 | 5.6 | 5.2 | 5.6 | 0.8 |
| 20 | 8.1 | 8.2 | 6.5 | 6.9 | 6.5 | 6.9 | 1.0 |
| 34 | 10.6 | 10.7 | 8.6 | 8.4 | 8.6 | 8.4 | 1.5 |
| 41 | 11.6 | 11.5 | 9.4 | 9.3 | 9.4 | 9.3 | 1.8 |
| 60 | 14.5 | 14.6 | 11.4 | 11.6 | 11.4 | 11.6 | 2.6 |
| 70 | 16.0 | 16.4 | 12.4 | 12.6 | 12.4 | 12.6 | 3.4 |

of water by the polysaccharide at the higher humidities is usually considered to be more complicated than that at lower humidities, the constants for the isothermals were calculated for each polysaccharide by using the experimental values up to a relative humidity of 65%. By this means it was hoped to obtain more satisfactory comparative values. The isotherm as written above is deduced from a theory which postulates (a) the formation of a solid solution of water in the polymer, and (b) the formation of a monohydrate between water and definite units of the polymer molecule. The water uptake is given by two terms, one corresponding to a Langmuir isotherm and the other to Raoult's equation for ideal solutions. The fraction of free dissolved water and that of water present as a monohydrate can be obtained at the various humidities by means of these two terms of the isotherm. This is shown for rabbit-liver glycogen in Fig. 1.

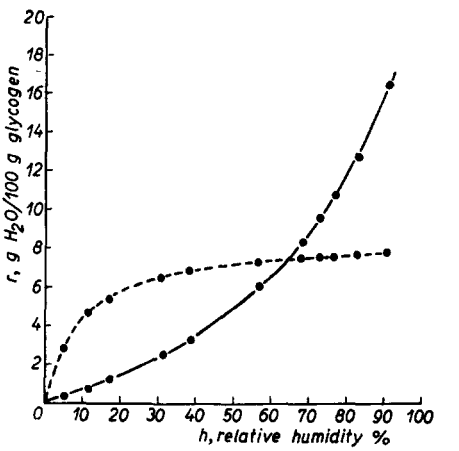


Fig. 1. The amount of free dissolved water —●——●— and water present as a monohydrate of glucose units --●---●---●-- in rabbit liver glycogen at various humidities. Calc. using the isotherm of HAILWOOD AND HORROBIN.

I

$r$ (%) AT 26°

$D$, experimental after desorption. $h$, relative humidity

| *Helix glycogen* | | *Leuconostoc dextran* | | | *Yeast mannan* | | | *Acetylated yeast glucan* | | *Acetylated yeast mannan* |
|---|---|---|---|---|---|---|---|---|---|---|
| $C$ | $S$ | $C$ | $S$ | $D$ | $C$ | $S$ | $D$ | $S$ | $D$ | $S$ |
| 3.2 | 3.1 | 2.8 | 2.6 | 5.0 | 2.9 | 2.8 | 2.8 | 0.3 | 0.4 | 0.2 |
| 5.7 | 6.1 | 5.0 | 5.2 | 7.6 | 4.7 | 5.0 | 6.0 | 0.5 | 0.9 | 0.7 |
| 7.1 | 7.3 | 6.3 | 6.6 | 9.5 | 5.6 | 5.8 | 6.9 | 0.8 | 1.3 | 1.0 |
| 9.8 | 9.6 | 8.8 | 8.8 | 12.2 | 7.6 | 7.6 | 8.8 | 1.2 | 2.1 | 1.6 |
| 11.0 | 11.0 | 9.8 | 9.6 | 13.4 | 8.6 | 8.6 | 10.2 | 1.5 | 2.7 | 2.0 |
| 14.2 | 14.2 | 12.6 | 12.7 | 15.8 | 12.3 | 12.3 | 13.9 | 2.8 | 4.2 | 2.9 |
| 16.3 | 16.5 | 14.3 | 14.4 | 17.0 | 15.7 | 14.3 | 15.7 | 4.0 | 5.4 | 3.8 |
| 18.5 | 18.3 | 15.9 | 17.3 | 18.0 | 20.3 | 16.9 | 17.2 | 5.2 | 6.8 | 4.4 |
| 20.1 | 21.6 | 17.2 | 21.3 | 21.2 | 24.8 | 19.9 | 19.9 | 6.6 | 8.8 | 5.2 |

*References p. 479.*

The constant $M$ represents the molecular weight of the section of the polymer molecule which is capable of uniting with one molecule of water to form a monohydrate. For the polysaccharides the smallest unit has a molecular weight of 162. Thus the fraction of units inaccessible to the water molecules for any hexose polysaccharide is given by $(M - 162)/M$ and this fraction for cotton has been correlated with the "crystalline portion" of the fibres, so that the fraction $(M - 162)/162$ represents the "crystalline to amorphous ratio" for a polysaccharide. These values have been calculated for the various substances investigated and are shown in Table IV.

From the values of $\alpha$ and $\beta$ for the various polysaccharides the standard free energy changes associated with (a) the solution of water in the polymer to give the solid solution, and (b) the combination of this dissolved water with the unhydrated polymer to form a hydrate, have been calculated, Table III. The standard states for these reactions are defined by HAILWOOD AND HORROBIN[3].

$$\text{(a) } \Delta F^\circ_{\text{soln.}} = -RT \ln 100\,\alpha$$
$$\text{(b) } \Delta F^\circ_{\text{chem.}} = -RT \ln \beta$$
$$\Delta F^\circ_{\text{Total}} = -RT \ln 100\,\alpha\beta$$

TABLE III

THE CONSTANTS OF THE HAILWOOD AND HORROBIN ISOTHERM AND THE FREE ENERGY CHANGES INVOLVED IN THE TWO PROCESSES OF HYDRATE FORMATION

$\Delta F_{\text{soln.}}$, solution of water in the polysaccharide, $\Delta F_{\text{chem.}}$, combination of dissolved water and unhydrated polysaccharide.

| *Substance* | *Constants of the* HAILWOOD AND HORROBIN *isotherm* | | | $+\Delta F^\circ_{soln.}$ | $-\Delta F^\circ_{chem.}$ | $-\Delta F^\circ_{total}$ |
|---|---|---|---|---|---|---|
| | $M$ | $\alpha$ | $\beta$ | *calories* | *calories* | *calories* |
| 1. 26° | | | | | | |
| Glycogens | | | | | | |
| Rabbit liver | 211 | 0.0072 | 14.27 (4) | 190 | 1570 | 1380 |
| Mytilus | 162 | 0.0052 | 10.00 (2) | 380 | 1360 | 980 |
| Helix | 175 | 0.0062 | 12.97 (1) | 280 | 1510 | 1230 |
| Yeast | 181 | 0.0057 | 11.67 (9) | 330 | 1450 | 1120 |
| Dextran (Leuconostoc) | 184 | 0.0057 | 11.87 (4) | 330 | 1460 | 1130 |
| Mannan (Yeast) | 289 | 0.0091 | 16.77 (8) | 60 | 1670 | 1610 |
| Glucan (Yeast) | 165 | 0.0071 | 11.07 (1) | 200 | 1420 | 1220 |
| 2. 45° | | | | | | |
| Glycogen rabbit liver | 156 | 0.0033 | 14.43 | 690 | 1680 | 990 |
| Glucan (Yeast) | 154 | 0.0050 | 13.94 | 430 | 1660 | 1230 |
| Dextran (Leuconostoc) | 156 | 0.0033 | 14.43 | 690 | 1680 | 990 |

TABLE IV

| *Substance* | *Fraction of glucose units inaccessible to the water molecules* $\frac{M - 162}{M}$ | *Crystalline to amorphous ratio* $\frac{M - 162}{162}$ |
|---|---|---|
| Glycogens | | |
| Rabbit liver | 0.23 | 0.30 |
| Mytilus | 0.00 | 0.00 |
| Helix | 0.07 | 0.08 |
| Yeast | 0.10 | 0.12 |
| Dextran (Leuconostoc) | 0.11 | 0.13 |
| Mannan (Yeast) | 0.44 | 0.78 |
| Glucan (Yeast) | 0.02 | 0.02 |

*References p. 479.*

*Heats and entropies of reaction.* For three polysaccharides the sorption of water has been studied at two temperatures. If it is assumed that the heat changes are independent of temp. over the range 26°–45°, the heats of the reactions and hence the entropy changes involved in the uptake of the water may be calculated. The results are shown in Table V.

TABLE V

THE HEAT AND ENTROPY CHANGES OF THE PROCESSES OF HYDRATE FORMATION
(For explanation of symbols see Table III)

| *Substance* | $-\Delta H^{\circ}_{soln.}$ *calories* | $+\Delta H^{\circ}_{chem.}$ *calories* | $-\Delta H^{\circ}_{Total}$ *calories* | $-\Delta S^{\circ}_{soln.}$ *calories/degree* | $+\Delta S^{\circ}_{chem.}$ *calories/degree* | $-\Delta S^{\circ}_{Total}$ *calories/degree* |
|---|---|---|---|---|---|---|
| Glycogen (Rabbit liver) | 7590 | 108 | 7482 | 26 | 6 | 20 |
| Glucan (Yeast) | 3410 | 2280 | 1130 | 12 | 12 | 0 |
| Dextran (Leuconostoc) | 5360 | 1920 | 3440 | 19 | 11 | 7 |

*Desorption isothermals.* These were experimentally determined on most of the materials investigated, and in all cases a hysteresis was observed, Table I. The period of exposure to the water vapour was extended to 400 h in some cases and no further decrease in weight was obtained, so that it seems that a true equilibrium condition had been reached.

## DISCUSSION

The interpretation of the water vapour isothermals of cotton, starch and proteins has been attempted by many authors who have applied isotherms based on several theories. Although no attempt to criticise these can be made in terms of the results obtained in this paper, a summary is useful since their application to a series of sorption results can give very similar information about the internal structure of the polymer. This, according to the isotherm adopted, may be calculated as "available adsorption surface" or "fraction of polymer units accessible to water molecules". The sorption is generally considered to be in two distinct stages: an initial strong adsorption of the Langmuir type which may incorporate compound formation as a hydrate; a secondary sorption which is interpreted either as a solution or an additional adsorption phenomenon.

*Adsorption theories.* 1. BRUNAUER, EMMETT AND TELLER[15] regarded the secondary stage of sorption as a multilayer adsorption phenomenon brought about by Van der Waals forces. At high humidities this adsorption might lead to capillary condensation. The isotherm developed by these authors has been applied to the water sorption of proteins, BULL[1] and of cotton, BABBITT[16]. 2. BRADLEY[17,18] thought that a multilayer adsorption could be caused by the induced or permanent dipoles of the first adsorbed molecules and the isotherm thus deduced was used by HOOVER AND MELLON[19] in their studies on proteins and cotton.

*Solution theories.* 1. PIERCE[20] derived an isotherm by considering the sorption of water by cotton to be an initial Langmuir adsorption and a secondary sorption of a less intimate manner resembling solution. 2. SIMHA AND ROWEN[21] and CUTLER AND MCLAREN[22] in work on cotton and proteins considered the initial sorption to be an adsorption phenomenon interpreted by the isotherm of BRUNAUER *et al.*[15], while the

*References p. 479.*

secondary sorption was regarded as a solution and the statistical treatment of FLORY[23] and HUGGINS[24] for polymer-liquid mixtures was applied. 3. HAILWOOD AND HORROBIN[3] treated the secondary sorption as an ideal solution of three species, anhydrous polymer, polymer hydrate and water. They applied their isotherm to cotton and proteins. Since most of the isotherms quoted fit the experimental results very well up to a relative humidity of about 70%, this is not a sufficient justification for the adoption of any one of them. The isotherm of HAILWOOD AND HORROBIN[3] has been applied to the results obtained in this work for the following reasons: 1. The formation of hydrates between the water molecules and the glucose units of cellulose has been shown by X-ray studies (HERMANS AND WEIDINGER[25]). 2. The constant $M$ seems to have some significance with regard to the structure of the polymer. In the calculations made in this paper the values for $M$, in some instances, become equal to the theoretical lowest value. 3. The information obtained from this constant for cotton has to some extent been satisfactorily related to other physical measurements such as density determinations (HERMANS[26]), heats of wetting and X-ray diffraction measurements (HERMANS[26]; HERMANS AND WEIDINGER[27,28]). 4. Calculations using the constant $M$ enable a quantitative comparison of the internal association of the preparations to be made for the various polysaccharides studied. 5. There is good agreement between the calculated and observed values for water uptake.

*Hydrate formation*

The initial uptake of water up to 20% relative humidity can be seen, from Fig. 1, to be mainly that due to monohydrate formation of the hexose units, and is undoubtedly associated with the available hydroxyl groups of the polysaccharide; since if these are blocked, as in the acetylated polysaccharides described above and in the work of WILSON AND FUWA[29] and SHEPPARD AND NEWSOME[30], the total amount of water sorption is considerably less, and no initial differentiation of the sorption curve indicating hydrate formation can be seen. Various workers on cotton (BABBIT[16]; SHEPPARD AND NEWSOME[31]; ASSAF, HAAS AND PURVES[32]), and on starch (SAIR AND FETZER[33]), have suggested that the sorption of water is due to the strong hydrogen bonding of the water on all three available hydroxyl groups of the glucose units. ASSAF *et al.*[32] stated that the initial sorption of water was due to association of the water molecules with the primary hydroxyl groups of each glucose unit, and the intermediate sorption at relative humidities between 10% and 40% was due to association of two more molecules of water with the two secondary hydroxyl groups; a trihydrate was thus visualised. In the work described in this paper with bacterial dextran, in which the principal linkage is 1:α:6 and few if any primary alcoholic groups are available, the sorption curve is essentially the same as that for the glycogens and other polysaccharides. It is suggested, therefore, that the monohydrate of the glucose units is associated with one or both of the secondary hydroxyls on carbon atoms 2 and 3 or 2 and 4. It is also apparent that a pair of adjacent secondary hydroxyl groups is not an essential feature for hydrate formation, since the isothermal of yeast glucan shows the compound formation.

The thermodynamic functions for hydrate formation have been calculated for the two processes involved. It is difficult to interpret these results further, since solution and subsequent hydrate production must involve complex reactions, with both the breakage of hydrogen bonds between the hydroxyl groups of the polysaccharides and the formation of hydrogen bonds between the dissolved water and the glucose units.

*References p. 479.*

*The internal structure of the polysaccharide preparations*

The sorption of water by starches was investigated by SAIR AND FETZER[33], who suggested that the differences in the secondary sorption amongst the various starches were caused by differences in the percentage available free hydroxyl groups. The idea that the water molecule could only penetrate the "amorphous" and not the "crystalline portion" of cotton fibres had been suggested by several lines of investigation and had been adopted by ASSAF *et al.*[32] in their calculations. The constant $M$ of the isotherm of HAILWOOD AND HORROBIN[3] allows the fraction of available glucose units to be calculated. This has been done for the polysaccharides investigated, and the results are discussed below.

Differences of approximately 0.5% in the percentage regain values can alter the value of $M$ by 30–40 units (*e.g.* yeast, rabbit-liver and mytilus glycogens), so that if the results are to be of value the % regains must be measured with an error of less than 0.2%. In the results quoted by HAILWOOD AND HORROBIN[3] the % regains are given to 0.01% although the data cannot always give this accuracy. The experimental work described here should permit a calculation of $M$ to approximately $\pm$ 15 units. It seems reasonable to suggest that the method of preparation and extraction of the polysaccharide will considerably affect the degree of internal association of the resultant product; this has already been fairly well established for cellulose preparations.

*The glycogens.* The calculated value of $M$ indicates a general open structure for these substances isolated by various methods. The yeast glycogen would seem to be the most compact and the value for the fraction of this glycogen inaccessible to water molecules is approximately 0.25.

*Yeast glucan.* The "crystalline to amorphous ratio" is very low, 0.02, although the preparation used in this work has not been broken down into a disorganised powder, since it still shows many structural features of the cell wall when it is examined under the optical and electron microscopes (NORTHCOTE AND HORNE[4]). The polysaccharide preparation is very insoluble in water. The insoluble nature of cellulose is explained in terms of the strong internal hydrogen bonding of the hydroxyl groups of the cellulose fibres, and in support of this view the value of $(M—162)/M$ for various cotton preparations is high (0.68; HAILWOOD AND HORROBIN[3]). The molecule of yeast glucan, in contrast to cellulose, is highly branched with the glucose units $1:\beta:3$ linked and a much weaker internal association appears to occur. The very insoluble nature of the glucan depends therefore on other factors, the most probable being that the molecule of glucan must be much larger than that of cellulose. The glycogens have values for the fraction $(M—162)/M$ which are very similar to that of glucan, but the glycogens are soluble. If molecular size is the factor which determines the solubility of these polysaccharides, as seems probable, the molecules of glucan must be even larger than those of glycogen (approx. $6 \cdot 10^6$).

*Dextran.* The calculated values of $M$ are similar to those of the glycogens. The primary hydroxyl group of carbon atom 6 of the glucose units of the polymers would thus seem to be of little influence in the general internal association of the polysaccharide preparation.

*Mannan.* The mannan preparation which is structurally very dissimilar from the glucose polysaccharides also seems to be much more internally associated than any of the other polysaccharide preparations.

*References p. 479.*

*The effect of temperature*

At the higher temperature the value of $M$ decreases to approximately the theoretical value, indicating that most of the polysaccharide has become available to the water molecules at this temperature. Generally, the amount of water sorbed at the lower humidities is unaffected by a rise in temperature, but the amount of secondary sorption is decreased.

*The desorption isothermals*

In all the preparations examined in this work the sorption-desorption isothermals show a hysteresis. This has been reported repeatedly for cotton and proteins, and has been discussed extensively by BARKAS[34]. The work shown here except as an extension of the phenomenon for the substances investigated adds no new information which could amplify or modify the theories which account for it.

SUMMARY

1. The sorption-desorption isothermals have been determined at 26° for rabbit-liver, yeast, helix, and mytilus glycogens, yeast glucan, yeast mannan and bacterial dextran. The sorption isothermals of glucan, liver glycogen and dextran were also determined at 45°.

2. The uptake of water by these polysaccharides has been interpreted according to an isotherm developed by HAILWOOD AND HORROBIN[3]. The values of the constants of this isotherm for the various substances have been used to calculate (a) the degree of internal association of the polysaccharide preparation, which is discussed in relation to solubility and molecular weight, (b) thermodynamic functions for the processes of solid solution and hydrate formation involved in water uptake.

3. A monohydrate between water and the hexose units of the polysaccharides is postulated, and evidence is presented that this water is associated with secondary hydroxyl groups of the hexose units.

RÉSUMÉ

1. Les isothermes de sorption-désorption à 26° des glycogènes de foie de lapin, de levure, d'hélix et de mytilus, des glucosanes de levure, des mannanes de levure et des dextranes bactériennes ont été déterminées. Les isothermes de sorption des glucosanes, du glycogène du foie et des dextranes ont été également déterminées à 45°.

2. L'adsorption d'eau par ces polysaccharides a été interprétée à l'aide d'une isotherme développée par HAILWOOD ET HORROBIN[3]. Les valeurs des constantes de cette isotherme pour les diverses substances ont servi à calculer (a) le degré d'association interne de la préparation de polysaccharide, qui est discuté en relation avec la solubilité et le poids moléculaire; (b) les fonctions thermodynamiques reliées à la formation de solution solide et d'hydrate qu'implique l'adsorption d'eau.

3. Il existerait un monohydrate entre l'eau et les unités hexoses des polysaccharides et cette eau serait associée à un groupe hydroxyle secondaire des unités hexoses.

ZUSAMMENFASSUNG

1. Die Sorptions- und Desorptionsisothermen wurden bei 26° für Kaninchenleber-, Hefe-, Schnecken- und Miesmuschelglycogen, Hefeglucan, Hefemannan und Bakteriendextran bestimmt. Die Sorptionsisothermen von Glucan, Leberglycogen und Dextran wurden auch bei 45° bestimmt.

2. Die Wasseraufnahme dieser Polysaccharide wurde wie eine von HAILWOOD UND HORROBIN[3] entwickelte Isotherme interpretiert. Die Werte der Konstanten dieser Isotherme für die verschiedenen Substanzen wurden benützt um (a) das Ausmass der inneren Assoziation des Polysaccharidpräparates, das in Bezug auf die Löslichkeit und das Molekulargewicht besprochen wird, und (b) die thermodynamischen Funktionen für die Prozesse der festen Lösung und der Hydratbildung, die sich bei der Wasseraufnahme abspielen, zu berechnen.

3. Ein Monohydrat von Wasser und Hexoseeinheiten der Polysaccharide wird postuliert und es wird augenscheinlich dargelegt, dass dieses Wasser mit den sekundären Hydroxylgruppen der Hexoseeinheiten verbunden ist.

*References p. 479.*

## REFERENCES


[1] H. B. BULL, *J. Am. Chem. Soc.*, 66 (1944) 1499.
[2] A. R. URQUHART AND A. M. WILLIAMS, *J. Text. Inst.*, 15T (1924) 433.
[3] A. J. HAILWOOD AND S. HORROBIN, *Trans. Faraday Soc.*, 42B (1946) 84.
[4] D. H. NORTHCOTE AND R. W. HORNE, *Biochem. J.*, 51 (1952) 232.
[5] D. H. NORTHCOTE, *Biochem. J.*, 53 (1953) 348.
[6] D. J. BELL, *J. Chem. Soc.*, (1948) 992.
[7] D. J. BELL AND D. J. MANNERS, *J. Chem. Soc.*, (1952) 3641.
[8] D. J. BELL, *Biochem. J.*, 30 (1936) 2144.
[9] E. BALDWIN AND D. J. BELL, *Biochem. J.*, 34 (1940) 139.
[10] D. J. BELL AND D. H. NORTHCOTE, *J. Chem. Soc.*, (1950) 1944.
[11] W. N. HAWORTH, E. L. HIRST AND F. A. ISHERWOOD, *J. Chem. Soc.*, (1937) 784.
[12] W. N. HAWORTH, R. L. HEATH AND S. PEAT, *J. Chem. Soc.*, (1941) 833.
[13] B. INGELMAN AND M. S. HALLING, *Ark. Kemi*, 1 (1949) 61.
[14] R. E. WILSON, *Ind. Eng. Chem.*, 13 (1921) 326.
[15] S. BRUNAUER, P. H. EMMETT AND E. TELLER, *J. Am. Chem. Soc.*, 60 (1938) 309.
[16] J. D. BABBITT, *Canad. J. Res.*, 20A (1942) 143.
[17] S. BRADLEY, *J. Chem. Soc.*, (1936) 1467.
[18] S. BRADLEY, *J. Chem. Soc.*, (1936) 1799.
[19] S. R. HOOVER AND E. F. MELLON, *J. Am. Chem. Soc.*, 72 (1950) 2562.
[20] F. T. PIERCE, *Shirley Inst. Mem.*, 8 (1929) 35.
[21] R. SIMHA AND J. W. ROWEN, *J. Am. Chem. Soc.*, 70 (1948) 1663.
[22] J. A. CUTLER AND A. D. MCLAREN, *J. Polymer. Sci.*, 3 (1948) 792.
[23] P. J. FLORY, *J. Chem. Phys.*, 10 (1942) 51.
[24] M. L. HUGGINS, *Ann. N.Y. Acad. Sci.*, 43 (1942) 1.
[25] P. H. HERMANS AND A. WEIDINGER, *J. Colloid Sci.*, 1 (1946) 185.
[26] P. H. HERMANS, *Contributions to the Physics of Cellulose Fibres.* Elsevier Pub. Co. Amsterdam–Brussels–London–New York, 1946.
[27] P. H. HERMANS AND A. WEIDINGER, *J. Am. Chem. Soc.*, 68 (1946) 2547.
[28] P. H. HERMANS AND A. WEIDINGER, *J. Am. Chem. Soc.*, 68 (1946) 1138.
[29] R. E. WILSON AND T. FUWA, *Ind. Eng. Chem.*, 14 (1922) 913.
[30] S. E. SHEPPARD AND P. T. NEWSOME, *J. Phys. Chem.*, 33 (1929) 1817.
[31] S. E. SHEPPARD AND P. T. NEWSOME, *Ind. Eng. Chem.*, 26 (1934) 285.
[32] A. G. ASSAF, R. H. HAAS AND C. B. PURVES, *J. Am. Chem. Soc.*, 66 (1944) 66.
[33] L. SAIR AND W. R. FETZER, *Ind. Eng. Chem.*, 36 (1944) 205.
[34] W. W. BARKAS, *Trans. Faraday Soc.*, 42B (1946) 137.


Received March 10th, 1953