

COMMUNICATIONS

The sorption of water vapour by starch and the application of the Young and Nelson equations

G. ZOGRAFI*, J. T. CARSTENSEN, M. KONTNY, F. ATTARCHI, *School of Pharmacy, University of Wisconsin, Madison, WI 53706, U.S.A.*

In a recent article (York 1981) water sorption and desorption isotherms of gelatin, maize starch and maize starch:barbital mixtures were obtained and analysed according to an approach developed by Young & Nelson (1967a). Young & Nelson attempted to relate equilibrium water vapour sorption and desorption with biological materials to relative humidity by assuming three basic mechanisms of water uptake into a biological cell: (1) a monomolecular layer of water on the outer surface of the cell; (2) multimolecular layers of water on top of the first layer; and (3) water absorbed within the cell. The approach used to derive appropriate equations was essentially the same as that used to derive the Langmuir and BET equations for vapour adsorption (Brunauer et al 1938) with an additional contribution by the absorbed water. In this regard, an important stipulation in this model is that water entry into and exit from the biological cell is determined by the amount of water bound to the outer cell surface. Young & Nelson concluded that the hysteresis observed in moisture sorption and desorption curves with such materials arises because absorbed moisture within the cell cannot be removed during desorption until sufficient water from the monolayer has been removed from the surface. Two equations were derived to describe total water sorption, M_s , and desorption, M_d , where:

$$M_s = A(\theta + \alpha) + B\phi \quad (1)$$

and

$$M_d = A(\theta + \alpha) + B\theta(RH_{max}) \quad (2)$$

The exact definition of each parameter is described by Young & Nelson (1967a), so it is sufficient to point out

Table 1. Various constants obtained for water sorption by wheat and maize starch from the Young & Nelson model.†

Material	A	B	E	Reference
Wheat	0.053	0.067	0.11	Young & Nelson (1967)
Wheat	0.050	0.067	0.10	This study
Maize starch	0.012	0.12	0.15	York (1981)
Maize starch	0.015	0.11	0.14	This study

† Simultaneous multiple regression analysis of sorption and desorption data, correlation coefficients in this study are all no less than 0.999.

* Correspondence.

that $A(\theta + \alpha)$ represents the contributions of monolayer and multilayer sorption, while the second term in each equation represents the absorbed water uptake. A third parameter which determines the values of θ and α directly, and ϕ indirectly, is E, where

$$E = \exp[-(q_1 - q_L)/kT] \quad (3)$$

The parameter, E, is analogous to the C term in the BET equation, where q_1 is the sorption energy of molecules bound to the surface of the cell and q_L is the energy of water condensation with itself, reflecting the energy associated with multilayer sorption.

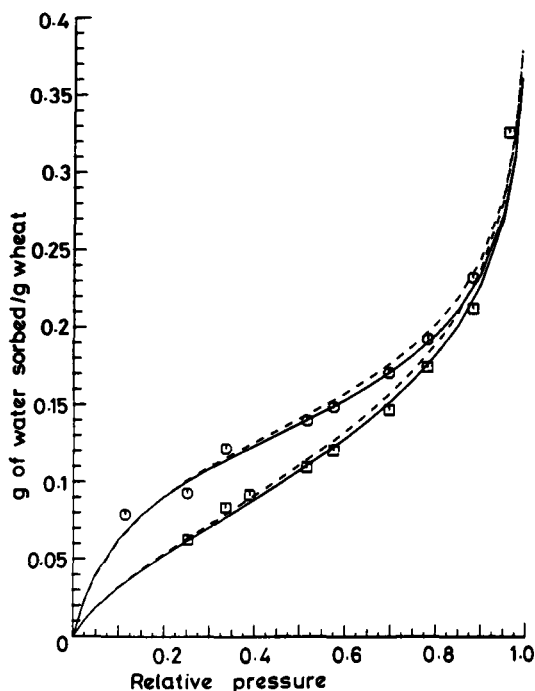


Fig. 1. Water vapour sorption and desorption isotherms for wheat. Experimental data: sorption (\square) and desorption (\circ) from Young & Nelson (1967b). Predicted from simultaneous fit of sorption and desorption data using Young and Nelson model: (----) Young & Nelson (1967b), (—) this study.

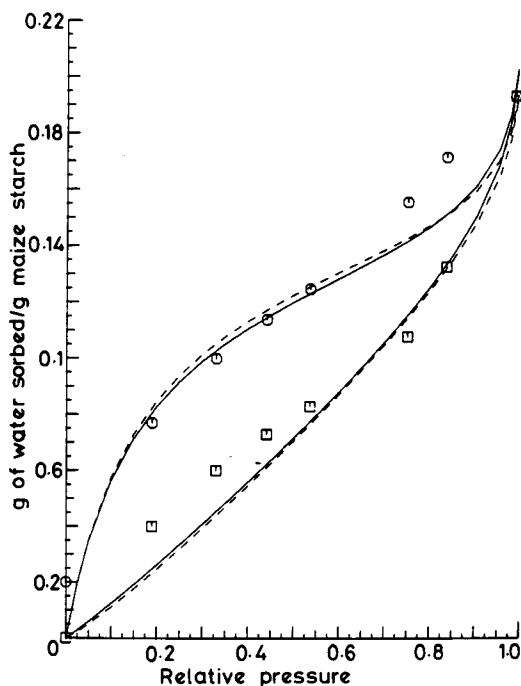


FIG. 2. Water vapour sorption and desorption isotherms for maize starch. Experimental data: sorption (\square) and desorption (\circ) from York (1981). Predicted from simultaneous fit of sorption and desorption data using Young & Nelson model: (----) York (1981), (—) this study.

By computer fit to both sorption and desorption data simultaneously, using three adjustable parameters, A, B, and E and multiple regression analysis, it was possible to obtain one set of constants describing equations 1 and 2. It was then possible to prepare separate isotherms for monolayer, multilayer and absorbed moisture using these constants and equation 1. Values of A, B, and E used by Young & Nelson (1967b) for their analysis of water sorption on wheat, and by York (1981) for maize starch, are given in Table 1. Also included in Table 1 are values obtained by the present authors using the same data and the same type of multiple regression analysis. Fits of these constants to reported data are also shown in Figs 1 and 2. Such comparisons were made to be sure that further analysis of other data in this study was consistent with that carried out by Young & Nelson (1967b) and York (1981).

In view of the great interest in establishing the nature of bound and unbound water in various pharmaceutical excipients such as starch, the application by York (1981) of the Young & Nelson model to such systems has great potential significance and deserves considerable attention and analysis. This is particularly important because the Young & Nelson model assumes that the system under consideration is a biological cell and that outer

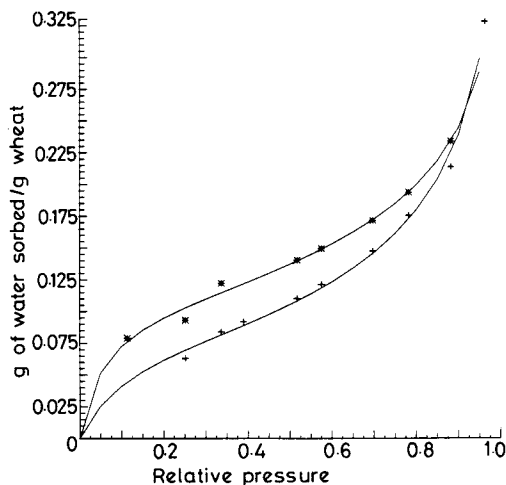


FIG. 3. Water vapour sorption and desorption isotherms for wheat. Experimental data: sorption (+) and desorption (*) from Young & Nelson (1967b). Predicted from individual fit of sorption and desorption data using Young & Nelson model: (----) York (1981), (—) this study.

sorbed and inner absorbed water can be clearly differentiated. Such a situation would not necessarily be expected with the starch grain, indeed, alternative models for water sorption by starch have been proposed. Gupta & Bhatia (1969), for example, have treated water sorption on starch in a manner similar to the physisorption of gases in porous solids, and have attributed hysteresis to capillary condensation and pore geometry. Van den Berg et al (1975), have proposed that water vapour uptake in the starch grain is almost entirely governed by the anhydroglucose residues of the starch polymer. They suggest a model which requires binding of water molecules homogeneously throughout the starch grain, first as a monolayer and then as a second layer. Any remaining water is taken up in a more nonspecific manner.

One possible approach toward assessing the significance of the Young & Nelson model is to analyse the physical meaning of the constants in equations 1 and 2. Since the term, A, is directly related to the volume of water sorbed in the monolayer for a completely covered surface, V_m , where

$$A = \frac{V_m \rho}{W} \quad (4)$$

and where W is the weight of dry sample and ρ is the density of water in the monolayer, A in the Young & Nelson model in the strictest sense, should correspond exactly to the external surface area per gram of solid. For a starch grain to take up water in a manner described in this model the monolayer should form around the outside of the starch grain and 'absorbed' water should enter into the starch grain. Thus the value of V_m/W for water sorption should be calculable from an

Table 2. Values of V_m/W for water sorption by various solids using the Young & Nelson model*

Starch	V_m/W ($\text{cm}^3 \text{g}^{-1}$)	Reference
Maize	0.015	York 1981
Maize	0.030	Wurster et al 1982
Maize	0.060	Hellman et al 1952
Maize	0.060	Sair & Fetzer 1944
Wheat	0.069	Van den Berg 1981

* Simultaneous fit of sorption and desorption data with a correlation coefficient of no less than 0.999 in all cases.

independently assessed specific surface area and the cross-sectional area of a water molecule in the monolayer (taken to be 10.6 \AA^2 per molecule; McClellan & Harnsberger 1967).

In Table 2 are listed values of V_m/W for water vapour sorption on maize and wheat starch obtained with 5 sets of data in the literature and applying the Young & Nelson model and equation 4. Assuming that maize starch has an average specific surface area of $0.48 \text{ m}^2 \text{ g}^{-1}$ and wheat starch, $0.22 \text{ m}^2 \text{ g}^{-1}$, as determined by nitrogen or krypton gas adsorption (Hellman & Melvin 1950; Radley 1953; Zografis 1960; Kontny 1983), the expected values of V_m/W for water sorption are about $13.5 \times 10^{-5} \text{ cm}^3 \text{ g}^{-1}$ for maize starch and $6.2 \times 10^{-5} \text{ cm}^3 \text{ g}^{-1}$ for wheat starch. These values are clearly at least two orders of magnitude smaller than the values

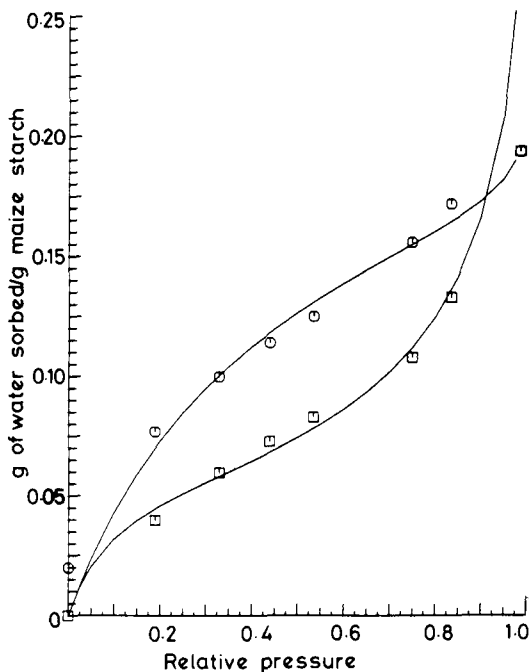


FIG. 4. Water vapour sorption and desorption isotherms for maize starch. Experimental data: sorption (\square) and desorption (\circ) from York (1981). Predicted from individual fit of sorption and desorption data using Young & Nelson model (—).

estimated from the Young & Nelson model. Note also the significant lack of agreement among the four studies dealing with maize starch despite the fact that computer fit of each set of data in itself was excellent. The reasons for this variation in experimental results are not clear.

The fact that water sorption on starch would lead to values of V_m/W which are much greater than the available external surface area of starch grains is not surprising since it is generally accepted that water enters the starch grain (Gupta & Bhatia 1969; Van Den Berg et al 1975). Indeed, if the BET equation, upon which equations 1 and 2 are based, is applied to water sorption on starch, as has been done by others, values of V_m/W should be of the same magnitude as obtained with the Young & Nelson model. Such values are given in Table 3 for the same systems analysed in Table 2. The values are similar, although the Young & Nelson results generally tend to be lower than those obtained using the BET equation.

As can be seen with the BET results, hysteresis between the sorption and desorption curves down to low values of relative humidity gives rise to two sets of values for V_m/W . The fact that one set of constants is obtained by the Young & Nelson approach has been suggested to be a major advantage of its use (Young & Nelson 1967ab). However, if these constants are physically meaningful they should describe the sorption and desorption curves when each set of data is also fitted individually by multiple regression analysis. Figs 3 and 4 show the fit to data for wheat and for maize starch done separately on the sorption and desorption curves. The fit is excellent when the best set of values for A, B, and E are used, however comparison of these values in Table 4 clearly shows some inconsistencies. First, in all cases values of the various constants are not the same for sorption and desorption, and second, values of A obtained by simultaneous fit of both curves are quite different from the corresponding values obtained by treating the curves separately.

Based upon this analysis, we would like to suggest that the use of the Young & Nelson model to describe the physical state of water vapour taken up by biological materials, like starch, may not be justified. As with other models which have attempted to fit such sorption isotherms with multiparameter equations, despite good fit to the data (Venkateswaran 1970; Van den Berg 1981), the physical significance of the results appears to

Table 3. Values of V_m/W for water sorption by various starch samples using the BET model.

Starch	V_m/W ($\text{cm}^3 \text{g}^{-1}$)		Reference
	Absorption	Desorption	
Maize	0.051	0.072	York 1981
Maize	0.083	0.099	Wurster et al 1982
Maize	0.078	0.095	Hellman et al 1952
Maize	0.066	0.087	Sair & Fetzer 1944
Wheat	0.085	0.138	Van den Berg 1981

Table 4. Various constants obtained for water vapour sorption by wheat and by maize starch from the Young & Nelson model. In all cases regression correlation was no less than 0.999.

Solid	A _{ADS}	A _{DES}	B _{ADS}	B _{DES}	E _{ADS}	E _{DES}	Reference
Wheat	0.080	0.060	-0.42	0.41	0.12	0.05	Young & Nelson 1976b
Maize starch	0.059	0.0074	-0.038	0.15	0.10	0.30	York 1981
Maize starch	0.022	0.024	0.18	0.15	10 ⁻⁷	0.14	Wurster et al 1982
Maize starch	0.047	0.050	0.086	0.086	10 ⁻⁴	0.12	Hellman et al 1952
Maize starch	0.054	0.043	0.071	0.10	0.015	0.11	Sair & Fetzter 1944
Wheat starch	0.022	0.014	0.23	0.25	2 × 10 ⁻⁵	0.47	Van den Berg 1981

be open to some question. In view of these uncertainties, and the very complex nature of this process, it would appear that methods independent of sorption isotherm analysis will have to be developed before we can gain a more thorough understanding of the thermodynamic state of water in such biological materials.

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J. Pharm. Pharmacol. 1983, 35: 458-459
Communicated December 10, 1982

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Comparison of the effects of nabumetone, a new anti-inflammatory drug, and indomethacin on arachidonic acid-induced hypotension in the rat

T. C. HAMILTON, SUSAN D. LONGMAN*, *Beecham Pharmaceuticals, Medicinal Research Centre, Coldharbour Road, The Pinnacles, Harlow, Essex, CM19 5AD, U.K.*

Endogenous vasodilator prostaglandins, such as prostacyclin, may play an important role in the regulation of vascular tone such that impairment of their synthesis leads to an unwanted increase in vascular resistance in specific beds (Dusting et al 1981). The recent report that a high intravenous dose of indomethacin, an acidic non-steroidal anti-inflammatory drug that inhibits prostaglandin synthesis, caused coronary vasoconstriction in patients with coronary artery disease, has highlighted this problem (Friedman et al 1981).

Nabumetone is a novel non-acidic anti-inflammatory drug which only weakly inhibits prostaglandin synthesis in-vitro (Boyle et al 1982). As such, nabumetone may cause less interference with the cardiovascular action of endogenous vascular prostaglandins than indomethacin and so we undertook a comparison of the effects of

these anti-inflammatory drugs on the hypotensive response to the prostaglandin precursor, arachidonic acid, in spontaneously hypertensive rats (SHR). This model was chosen since Dusting et al (1981) have recently shown that the secondary phase of the hypotensive response to arachidonic acid is dependent on its conversion to vasodilator prostaglandins.

Method

Groups of 6 male spontaneously hypertensive rats (SHR) (300-400 g), derived from the Japanese strain (Okamoto & Aoki 1963), were pretreated orally with nabumetone (20 or 50 mg kg⁻¹), indomethacin (1.5 mg kg⁻¹) or vehicle and anaesthetized 2-2½ h later with pentobarbitone sodium (60 mg kg⁻¹ intraperitoneally). The choice of pretreatment period and doses of drug was based on the time course and relative ability

* Correspondence.