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Reinvestigation of Potato Starch Volume during the Sorption Process

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SUMMARY

A thorough reinvestigation of the dependence of the specific volume of potato starch on water ad- and desorption is described. Measurements by toluene pycnometry show that hysteresis only occurs between 0 and 13% H_2O *(dry solids basis). The results are interpreted in terms of a progressive filling of intergranular voids by water molecules of equivalent constant density. Other results give information on bulk starch density, thermal expansion coefficients, the influence of different immersion liquids and the effect of the different physical states of starchy products (dry gels and acid hydrolysed fractions).*

1. INTRODUCTION

The physical properties of macromolecular materials of plant origin are very dependent on water ad- or desorption. Volume dependent properties are especially informative when considering the structural interpretation of hydration (which involves the global swelling of the matrix and changes in chain packing). In previous studies, Buleon *et al.* (1982) have shown that the apparent crystallinity of potato starch granules changes in parallel with the density as measured by an air pycnometric method.

Because of the uncertainty underlying these latter measurements on products with various water contents and the influence of sorption hysteresis, we have conducted a more precise determination by classical

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liquid pycnometry in order to minimize the alteration of the original state of hydration. The changes in density have been correlated with water content, hysteresis, different degrees of crystallinity of materials and temperature.

In a recent publication dealing with water–starch interactions, van den Berg (1981) has reviewed the literature covering physicochemical measurements. He has pointed out the difficulties in interpreting volume dependent properties at the microscale since interaction between hydrated starch and the pycnometric fluid cannot be avoided. The present work improves the precision of available data and demonstrates the limited influence of sorption hysteresis on specific volume.

2. MATERIALS AND METHODS

2.1 Sample preparation

2.1.1 Native potato starch

'Native' granules were obtained directly from potatoes by wet grinding, decanting, washing, sieving and mild drying (50°C) in thin layers.

2.1.2 Hydrolysed starches

Lintnerized amylodextrins were prepared by the hydrochloric acid hydrolysis method employed by Robin *et al.* (1975). Nägeli amylodextrins were prepared by a method adapted from the sulphuric acid hydrolysis procedure of Kainuma & French (1971).

(i) Preparation of lintnerized amylodextrins: Starch (200 g) was left for 35 days at 35°C in 2 litres 2·2 N hydrochloric acid. After centrifugation the residue was washed with distilled water and dialysed until chloride ions could no longer be detected by silver nitrate. After drying under vacuum at 50°C, the product was dissolved in hot water, precipitated in methanol and then recrystallized. Longer acid treatment gave a crystalline fraction with monodisperse, short amylose chains (DP = 15).

(ii) Preparation of Nägeli amylodextrins: 2 litres of 16% sulphuric acid were mixed with 50 g starch and left at 25°C for 90 days; the granules were shaken daily. Washing and drying was then carried out as described above.

2.1.3 Gelatinized starch

In order to avoid freeze drying and at the same time to have small, well defined particles, a portion of 5% gel obtained by heating at 100°C for 30 min with strong agitation was dried on a heated plate at 90°C. The resulting film was ground to a particle size of 200 μm.

2.2 Water vapour sorption

All samples were brought to the desired state of hydration by vapour phase sorption at 25°C for at least one week using the classical method (a desiccator under vacuum with saturated salt solutions or sulphuric acid; Multon *et al.*, 1980). The corresponding sorption isotherm is given in Fig. 1. Before adsorption, the samples were predried to constant weight *in vacuo* over P_2O_5 as desiccant. Desorbed samples were obtained by conditioning after thorough wetting of the granules. Water content determinations were made using a normalizing method,* i.e. 130°C, 1 h 30 min; this is considered to leave 0·1% H_2O in comparison to dehydration over P_2O_5 but no correction was applied.

2.3 Specific volume determinations

The liquid pycnometry method of Schoch & Leach (1964) was used with minor modifications. Samples (~3 g) were immersed in two stages in a 23·5 ml pycnometer; great attention was given to degassing under saturating water vapour pressure. Final volume adjustment was performed while the pycnometer remained immersed in a water bath regulated at 10, 25 or 40°C ± 0·1°C. High quality ground glass fittings were required to avoid evaporation. The liquids used were toluene, water and methanol; in the latter case, because of methanol's low boiling point, degassing was required for 1 h with frequent agitation under atmospheric pressure. The weight was determined to ± 0·01 mg.

Five replicates for each sorption level gave an experimental accuracy of $\pm 4 \times 10^{-4}$ g cm^{-3} on adsorption and $\pm 8 \times 10^{-4}$ g cm^{-3} on desorption (at 95% confidence level). However, samples with an a_w higher than 0·96 were discarded because of the excessively wide spread of results (we suspect intergranular condensation).

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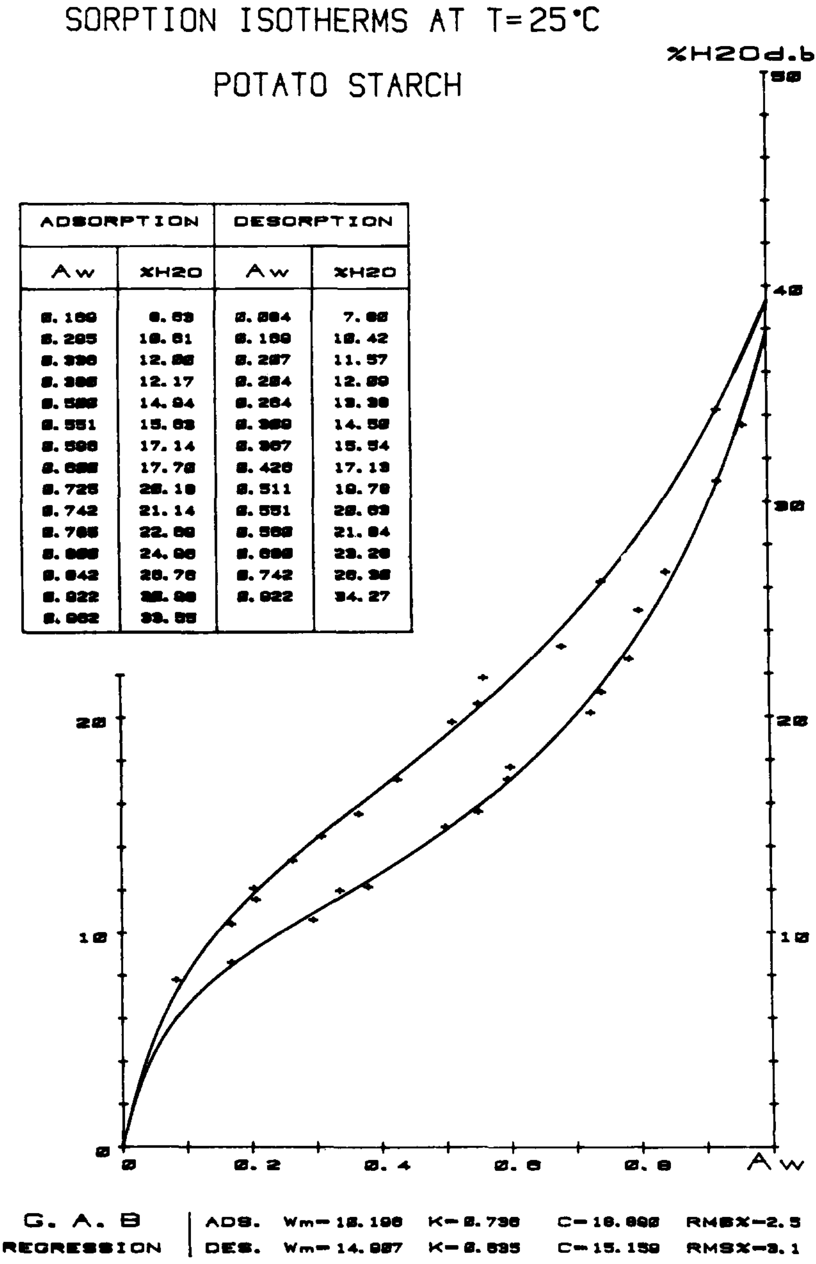
*Norme Afnor NF V 03 708 (1979), Tour Europe Cédex 07, 92080 Paris La Defense.



ADSORPTION		DESORPTION	
Aw	xH2O	Aw	xH2O
0.160	8.83	0.084	7.66
0.285	10.61	0.160	10.42
0.330	12.06	0.207	11.57
0.386	12.17	0.234	12.69
0.500	14.94	0.264	13.36
0.551	15.63	0.360	14.56
0.596	17.14	0.367	15.54
0.686	17.76	0.426	17.13
0.725	20.10	0.511	18.76
0.742	21.14	0.551	20.63
0.765	22.60	0.560	21.84
0.806	24.96	0.686	23.26
0.842	26.76	0.742	26.36
0.922	32.06	0.922	34.27
0.962	33.55		

Fig. 1. Ad- and desorption data smoothed by Guggenheim-Anderson-de Boer model (W_m = primary adsorbed fraction; for details, see Buleon *et al.*, 1982).

In order to express more clearly the inherent variation of the starch granule volume we used the expression proposed by Hermans (1952) for cellulose:

$$V(h) = (1 + h)/\rho_A^{(h)} \qquad (1)$$

where $V(h)$ = the measured volume referred to 1 g dry starch containing h g H_2O, h = the water fraction on a dry weight basis in g H_2O g^{-1} dry matter, $\rho_A^{(h)}$ = the specific gravity of starch containing h g H_2O. The uncertainty in experimental results, taking into account the water content, was always lower than $\pm 2 \times 10^{-3}$ (cm^3 g^{-1} dry basis + h g H_2O).

3. RESULTS AND DISCUSSION

3.1 Starch volume related to water content and hysteresis

Specific gravity results are shown in Fig. 2. The hysteresis effect is apparent in the range 0–13% H_2O (dry basis).

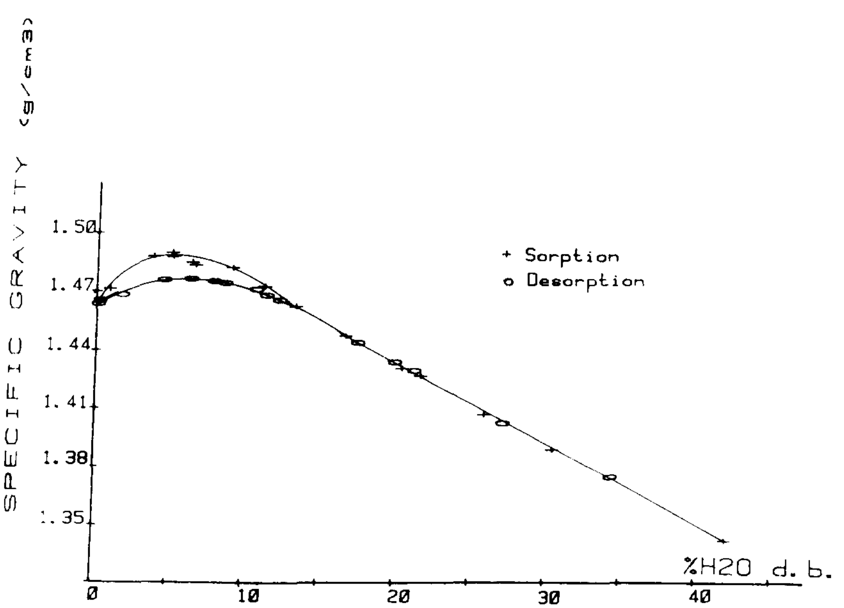


Fig. 2. Specific gravity as a function of the state of hydration (toluene liquid pycnometry).

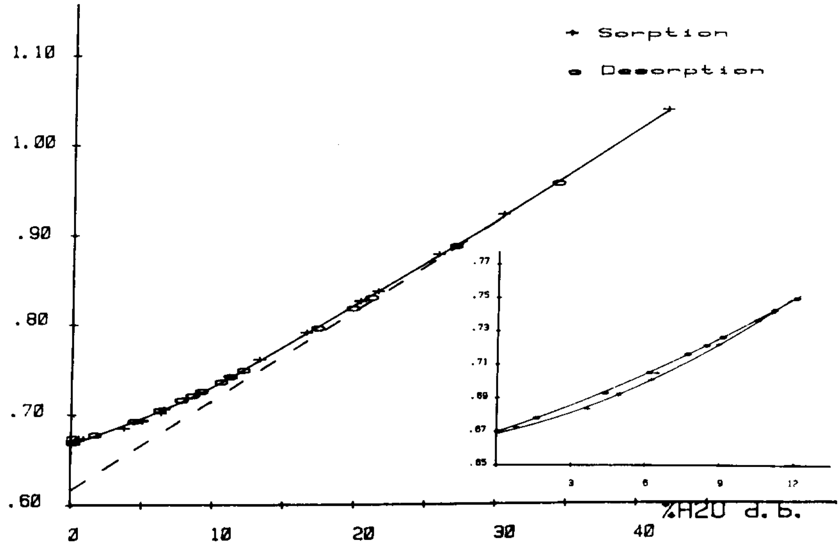


Fig. 3. Specific volume of 1 g dry starch as a function of water content.

In Fig. 3, the 1 g dry starch basis representation reveals more clearly the continuous swelling of the system. Three distinct regions are identified using polynomial regression smoothing:

(a) $0 < h < 0{\cdot}13$ dry basis

$$V_s(h) = 0{\cdot}668 + 0{\cdot}344h + 0{\cdot}027h^2 \quad \text{(for adsorption)} \qquad (2)$$

$$V_d(h) = 0{\cdot}669 + 0{\cdot}487h + 0{\cdot}015h^2 \quad \text{(for desorption)} \qquad (3)$$

(b) $0{\cdot}13 < h < 0{\cdot}30$

$$V(h) = 0{\cdot}632 + 0{\cdot}9432h \qquad (4)$$

(c) $h > 0{\cdot}30$

$$V(h) = 0{\cdot}614 + 1{\cdot}003h \qquad (5)$$

Correlation coefficients for these regressions are always better than 0·98.

Generally speaking $V(h)$ can be expressed as the sum of three partial volumes.

$$V(h) = V_s(h) + V_v(h) + h\dot{V}_w(h) \qquad (6)$$

with $V_s(h)$ = the volume occupied by the amylose and amylopectin chains, $V_v(h)$ = the volume of the 'empty' space between these chains and $\dot{V}_w(h)$ = the mean, specific volume of sorbed water.

The interpretation of these partial parameters has been widely discussed; here, we will follow Matthews' (1974) hypothesis by considering $\dot{V}_w(h)$ to be constant over the whole range of water contents and equal to that of pure water at temperature, $T(V_w^T)$; $V_s(h)$ will also be taken as constant. In this case, eqn (6) becomes:

$$V(h) = V_s + V_v(h) + hV_w^T$$

with $V_w^{25} = 1{\cdot}0028\ \mathrm{g\ cm^{-3}}$; V_w^{25} is the specific volume of water at 25°C (Weast, 1982). We should also remember that toluene measures only the volume confined by a wettable surface probably including only coarser capillaries if they exist.

In region (a) the swelling is limited through mutual compensation arising from an increase in the water volume fraction hV_w and a decrease in the voids volume $V_v(h)$; it is not surprising therefore that the specific gravity in Fig. 2 shows a maximum value at 5% H_2O (dry basis). The pronounced hysteresis leads to a higher volume for desorbing as compared with adsorption samples, but this vanishes at water contents above 13% H_2O (dry basis) while sorption hysteresis is still increasing at this point before decreasing near saturation (Fig. 1). Swelling is related to the rearrangement of hydrogen bonding between polysaccharide chains and it is very likely that a delay in shrinking preserves more void space on desorption. Sorption hysteresis should not be interpreted solely in terms of hindered swelling because there are other identifiable phenomena occurring over a range of water contents. For example, structural fluctuations remain possible well under the glass transition point which is considered by van den Berg (1981) to be around 15% H_2O dry basis at ambient temperature.

In region (b) voids must progressively fill up while granular swelling becomes more important. Here the linear relationship is rather well established but can only be interpreted as a reversible volume compensation between $V_v(h)$ and a fraction of hV_w^{25} since the slope differs significantly from the water specific volume.

In region (c), all voids have disappeared and eqn (7) becomes $V(h) = V_s + hV_w^{25}$ which yields $V_s = 0{\cdot}614\ \mathrm{cm^3\ g^{-1}}$ for starch in the swollen state. This value, when compared with dry starch granules with specific volume $V(o) = V_s + V_v(o) = 0{\cdot}670\ \mathrm{cm^3\,g^{-1}}$, gives a total void volume fraction of 9·12% of the volume of the polysaccharide chains.

Matthews' (1974) hypothesis which is used here for interpretation is based on Cohn and Edsall's work on electrostriction and Casper's treatment of the influence of hydrophobic groups. Most other authors who have studied the density of hydrated products prefer other interpretations. Gur-Arieh (1964) also found three distinct regions for wheat flour specific volume but he considered the sorbed water to have a greater density in the lower moisture range. The density of the water was determined as 1·48 at 0·7% H_2O (dry basis), 1·11 between 7 and 14% H_2O (dry basis) but decreased to 0·97 at saturation. Duprat (1974) supposed that starch granules had no 'voids' and that sorbed water on a molecular scale was under 'high compression' at lower activities; similarly, De Willigen & De Groot (1967) calculated a relative compression of the starch–water system at different hydrations. Volarovich *et al.* (1975) presented surprising and rather different results which attributed a density lower than 1 for water up to 9% H_2O (dry basis) but their measuring technique (helium pycnometry) was questionable because of the inaccessibility of microcavities (a similar idea is put forward by Gregg & Sing (1967) from sorption isotherms calculations). Their final conclusions agreed with those of Hermans (1952) since they showed that water can reach some regions where other gases or solvents cannot penetrate. Nevertheless, it is worth mentioning that the existence of water with a specific gravity 3% lower than that of the bulk liquid has been encountered in rigid mineral matrices such as silica gel (Etzler & Fagundus, 1983) and explained by a model of interfacial water structure.

Concerning the results themselves our figures are very comparable to those of de Willigen & de Groot (1967) whose study was limited to desorbing samples in the range 11–40% H_2O (dry basis). However, there is a small systematic discrepancy, their values for volume lying some $0{\cdot}006\ \mathrm{cm^3\,g^{-1}}$ lower. This can be attributed to either experimental conditions (sample drying, immersion liquid) or varietal fluctuations.

Comparing these results with those previously reported and derived from (Buleon *et al.*, 1982) the same general trend is observed, but in the previous work the hysteresis in specific gravity was observed up to 30% H_2O (dry basis) and the value for dry starch was $1{\cdot}483\ \mathrm{g\,cm^{-3}}$ instead of $1{\cdot}491\ \mathrm{g\,cm^{-3}}$. These differences are probably due to the lower precision ($\pm 5 \times 10^{-3}\ \mathrm{g\,cm^{-3}}$) and systematic error resulting from eventual condensation of water vapour during compression. A comparable tendency has been observed by Bushuk & Hlynka (1960) who found a hysteresis in specific gravity over the whole water content range when studying wheat kernels by toluene pycnometry.

Finally, Hellmann *et al.* (1952), who observed potato starch granule swelling by light microscopy, did encounter average diameter hysteresis for all water contents, desorbing samples having higher volumes.

In a parallel study dealing with the measurement of the diffusion coefficient, we have determined the average bulk product volume for different hydration levels. The technique only required a calculation of the volume of starch pellets of known weight and sorption state after weak compression (2 kg cm^{-2}) in an infrared dye.

Figure 4 confirms the hysteresis at low water contents found from the pycnometric data and allows the calculation of intergranular macroporous volume by comparison with Fig. 3.

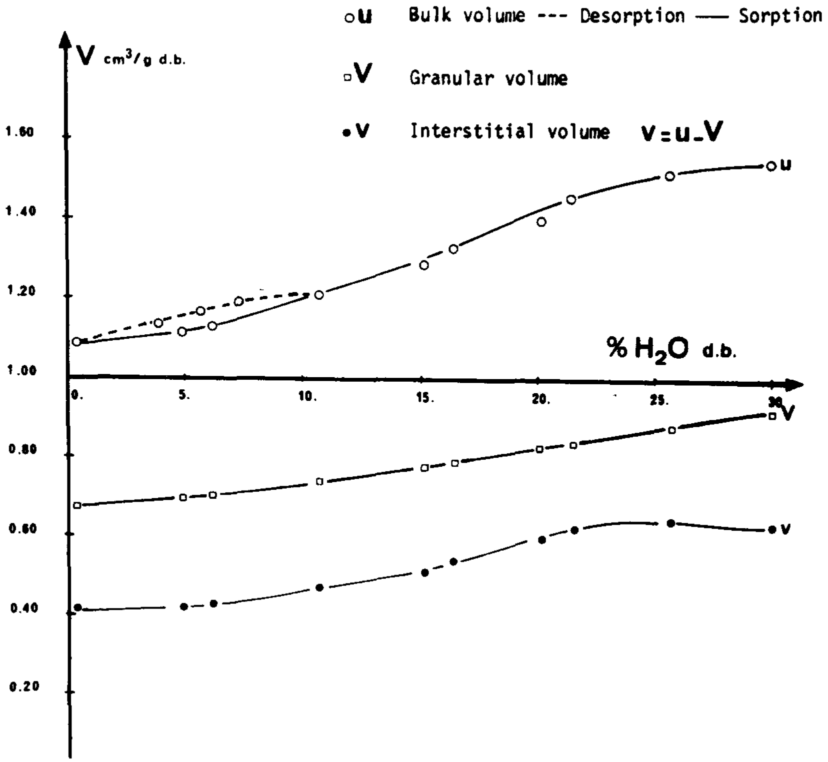


Fig. 4. Volume of 1 g dry starch as a function of water content.

In summary, we consider that during adsorption water molecules penetrate preferentially the voids contained in the starch granules; the macromolecular network undergoes only limited swelling as long as we remain in a kind of glassy state (van den Berg, 1981); with increasing water content rubbery behaviour appears associated with a larger expansion. With water contents over 30% H_2O (dry basis), no more voids persist and pure additivity of partial volumes is observed. A higher specific volume during desorption is limited to water contents lower than 13% H_2O (dry basis) which is about the quantity necessary to saturate primary adsorption sites (Buleon *et al.*, 1982). This can be related to some other interesting observations:

- an enhancement of X-ray apparent crystallinity which is only evident above this water content;
- a relative enhancement of sorption scanning curves (to be published);
- the lack of sorption hysteresis for a_w fluctuation limited to the range 0–0·2 (van den Berg, 1981).

At low water contents, the starch matrix is rather like a rigid solid, recovery from the fully swollen state occurring slowly by the 'collapsing' of high energy hydrogen bonds while at higher water contents structural rearrangements are easier.

3.2 Influence of immersion liquids

Three different immersion liquids have been tested on dry starch samples (Table 1).

TABLE 1

Dry Starch Specific Volume and Specific Gravity for Different Immersion Liquids

Immersion liquid	$\rho (g\ cm^{-3})$	$V = \frac{1}{\rho}\ cm^3\ g^{-1}$	r^a (Å)
Toluene	1·4931	0·6697	6·32
Water	1·6452	0·6078	3·85
Methanol	1·6480	0·6068	4·31

[a] Molecular radii calculated from specific volume data and assuming compact hexagonal packing.

The much lower specific gravity found in toluene is consistent with van den Berg's (1981) analysis. The measured volume in this case is likely to be somewhere between the volume of the macromolecular chains and the volume defined by the external surface of the starch granules observed at small magnification. Only large pores will be accessible to toluene which is sterically too large to penetrate all 'voids'.

In contrast, water is able to reach all hydroxyl groups including the crystalline areas in the granule. This was shown by Hennig (1977) who obtained complete isotopic exchange by heavy water. The identical specific volume in methanol indicates that this small molecule has a similar accessibility to that of water and has comparable hydrogen bonding capabilities. However, the easier degassing suggests that methanol has better wetting properties.

The bulk volume of dry starch immersed in these two liquids inside calibrated tubes gave values of 1·80 $cm^3 g^{-1}$ dry starch in water and 1·51 $cm^3 g^{-1}$ dry starch in methanol after 12 h sedimentation and 3 h degassing while it is close to 1·05 $cm^3 g^{-1}$ in toluene. Thus complete swelling is more limited in methanol than water; these aspects will be further investigated with respect to the polarity of swelling agents.

3.3 Influence of starch structural modifications

Table 2 summarizes the data for gelatinized and acid hydrolysed products in the dry state before immersion.

The highest values for the dried gel particles in toluene must be indicative of a vitreous state which is more compact after plate drying (90°C) than the native or organized state. There is no significant difference between the native and lintnerized samples but the Nägeli type is slightly denser and optical microscopy reveals large capillaries probably providing access to internal voids.

In water, the specific gravity decreases with enhanced 'X-ray crystallinity', i.e. from gel (amorphous) to native and hydrolysed. This suggests a less compact arrangement of crystalline domains in the hydrated compared to the amorphous state.

Although higher density is generally attributed to more ordered systems (Hermans, 1952) other authors, like Cleven *et al.* (1978) and Sarko & Wu (1978), have calculated theoretical densities of B type hydrated amylose crystals which would be 1·473 and 1·40 $g\ cm^{-3}$,

TABLE 2
Specific Volume of 1 g Dry Starch and Specific Gravity at 25°C for Different Structural Modifications

Samples	*Immersion liquid*			
	Toluene		*Water*	
	ρ *(g cm^{-3})*	*V (cm^3 g^{-1})*	ρ *(g cm^{-3})*	*V cm^3 g^{-1})*
Native potato starch	1·4931	0·670	1·6452	0·608
Nägeli (B)[a]	1·4985	0·667	–	–
Lintner (B)[a]	1·4939	0·669	1·6235	0·616
Hot plate dried gel	1·5077 1·5037	0·663 0·665	– –	– –
Recrystallized $\overline{DP}$ = 15 (A)	–	–	1·6206	0·617

[a] Crystalline type A or B.

respectively, instead of our value of 1·650 g cm^{-3}. In fact, these figures and those of Nara (1979) are hardly comparable since they result from calculation in the first two cases or from measurement on only partially crystalline products; the crystallinities have not yet been measured on an absolute scale for B type crystals. For the A type DP = 15 samples, recrystallized in methanol, the value of 1·620 g cm^{-3} is rather similar to that value of 1·56 for pure amylose calculated by Sarko & Wu (1978).

Once again information on the fine structure of the granule which would permit a precise interpretation of the macroscopic properties is missing, particularly when the materials under consideration are fractions or products derived from the native granule. Since sorption mechanisms act at the molecular scale between dispersed absorbant molecules (polydisperse amylose and amylopectin chains which may be partially crystalline) more specific (spectroscopic) methods are needed to fully characterize these mechanisms.

3.4 Influence of temperature

Table 3 summarizes the results of measurements at three water contents and three temperatures.

TABLE 3

Toluene Pycnometry Results at Different Temperatures and Water Contents

Temperature (°C)	*0% H_2O (dry basis)*			*4·91% H_2O (dry basis)*			*30·26% H_2O (dry basis)*		
	ρ *($g\ cm^{-3}$)*	V *($cm^3\ g^{-1}$)*	Δ *($cm^3 (g\ °C)^{-1}$)*	ρ *($g\ cm^{-3}$)*	V *($cm^3\ g^{-1}$)*	Δ *($cm^3 (g\ °C)^{-1}$)*	ρ *($g\ cm^{-3}$)*	V *($cm^3\ g^{-1}$)*	Δ *($cm^3 (g\ °C)^{-1}$)*
10	1·5116	0·662		1·5420	0·680		1·4187	0·918	
			5×10^{-4}			8×10^{-4}			1×10^{-4}
25	1·4931	0·670		1·5164	0·692		1·4172	0·919	
			2×10^{-4}			3×10^{-4}			
40	1·4878	0·672		1·5082	0·696		1·4170	0·919	

TABLE 4
Expansion Data of Water Saturated Potato Starch Obtained by Water Pycnometry

Temperature (°C)	*ρ (g cm^{-3})*	*V (cm^3 g^{-1})*
10	1·6517	0·605
25	1·6452	0·608
40	1·6382	0·610

The interpolated expansion coefficients, Δ, in cm^3 (g °C)$^{-1}$, are positive and vary in each range observed but they tend towards zero at higher hydration levels (30% H_2O (dry basis)). For drier conditions, the values compare well between 16 and 25°C with those of Rodewald (quoted by van den Berg, 1981) (for wheat starch, 4×10^{-4} cm^3 (g °C)$^{-1}$) and Fish (1957) ($2{\cdot}5 \times 10^{-4}$ cm^3 (g °C)$^{-1}$ for potato starch gel). In contrast, de Willigen & de Groot (1967) found a negative expansion coefficient ($-2{\cdot}8 \times 10^{-3}$ (g °C)$^{-1}$) between 0 and 45°C after extrapolation of heat of adsorption and specific gravity data to the fully hydrated state.

In order to check their theory, we made water pycnometric determinations at the same three temperatures (Table 4). The results showed a constant positive expansion coefficient $\Delta_{sat} = 4 \times 10^{-4}$ cm^3 (g °C)$^{-1}$, that of water being $1{\cdot}6 \times 10^{-4}$ cm^3 (g °C)$^{-1}$. This tendency is consistent with the usual increase in water sorption at higher temperatures for a given water activity and also illustrates the importance of low temperature spin drying in industrial processes.

CONCLUSION

The results presented here have shown surprisingly that the hysteresis effect is limited to low water contents. No easy interpretation of macroscopic measurement, such as volume, is possible in terms of molecular interactions. Even the influence of apparent crystallinity is not clear and further measurements will be made only on synthetic pure crystalline material since starch granules are still too complex systems for structural studies.

However, we may note that apparent volumes of amylose and amylopectin chains are almost identical in water and pure methanol (0·608–0·607 $cm^3\,g^{-1}$). The three different phases observed during swelling – (i) 0–13% H_2O (dry basis) with large apparent compression and hysteresis; (ii) 13–30% H_2O (dry basis) with weak apparent compression; and (iii) over 30% H_2O with additivity of water and starch volumes – have not yet been correlated with other physical properties (although X-ray crystallinity is absent in the first region).

REFERENCES

Buleon, A., Bizot, H., Delage, M. M. & Multon, J. L. (1982). *Die Stärke* **34**, 361.

Bushuk, W. & Hlynka, I. (1960). *Cereal Chemistry* **37**, 390.

Campbell, W. B. & Russel, J. K. (1934). *Quarterly Review, F.P.L. of C.* 24.

Cleven, R., van den Berg, C. & van der Plas, L. (1978). *Die Stärke* **30**, 223.

de Willigen, A. H. A. & de Groot, P. W. (1967). *Die Stärke* **19**, 368.

Duprat, F. (1974). Unpublished results.

Etzler, F. M. & Fagundus, D. M. (1983). *J. colloid. Interface Sci.* **93** (2), 585.

Fish, B. P. (1957). *Diffusion and Equilibrium Properties of Water in Starch*, Technical Paper 5, HMSO, London.

Gregg, S. & Sing, K. (1967). *Adsorption, Surface Area and Porosity*, Academic Press, London.

Gur-Arieh, C. (1964). *Diss. Abstract* **25**, 399.

Hellmann, N. W., Boesch, T. F. & Melvin, E. H. (1952). *J. Am. Chem. Soc.* **74**, 34.

Hennig, H. J. (1977). *Die Stärke* **29**, 289.

Hermans, P. H. (1952). Contribution à l'étude physique des fibres cellulosiques. *Bibliothèque des Industries Papetières*, Dunod, Paris.

Kainuma, K. & French, D. (1971). *Biopolymers* **10**, 1673.

Matthews, B. W. (1974). *J. Mol. Biol.* **82**, 513.

Multon, J. L., Bizot, H. & Martin, G. (1980). Techniques d'analyse et de contrôle en IAA, *Technique et Documentation APRIA*, Vol. 4, Lavoisier, Paris, pp. 1-60.

Nara, S. (1979). *Die Stärke* **31**, 73.

Robin, J. P., Mercier, C., Duprat, F., Charbonniere, R. & Guilbot, A. (1975). *Die Stärke* **27**, 35.

Sarko, A. & Wu, H. (1978). *Die Stärke* **30**, 73.

Schoch, J. J. & Leach, H. W. (1964). *Methods in Carbohydrate Chemistry*, Vol. IV, ed. R. L. Whistler, Academic Press, New York, pp. 101-3.

van den Berg, C. (1981). Thesis, Agricultural University, Wageningen, The Netherlands.

Volarovich, M. P., Gamayunov, N. I. C., Vasil'eva, Yu. L., Vasile'eva, M. yu. (1975). *Kolloidnyi Zhurnal* **37**, 345.

Weast, R. C. (1982). *Handbook of Chemistry and Physics*, CRC Press, Florida.