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EFFECT OF HYDROSTATIC PRESSURE ON STARCH GELATINISATION, AS DETERMINED BY DTA

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ABSTRACT

A study of starch gelatinisation over the pressure range 0·1–400 MPa has been performed using high pressure differential thermal analysis (HPDTA). The results show that the gelatinisation temperature first increases by a few degrees, becomes constant at 150–250 MPa and then decreases slightly. ΔH decreases with an increase in pressure, with the decrease being more rapid for wheat and smooth pea starches than for potato starch. Using the Clapeyron equation it can be deduced that ΔV is initially positive, but decreases with an increase in pressure to become zero at 150–250 MPa and eventually just negative.

INTRODUCTION

In two recent papers (Thevelein *et al.*, 1981 and Muhr & Blanshard, 1982) the changes induced in birefringence on subjecting starch granule/water mixtures to predetermined pressures and temperatures have been reported.

Application of the Clapeyron equation

$$\left.\frac{\partial T}{\partial P}\right|_{\Delta G=0} = \frac{T\,\Delta V}{\Delta H} \qquad (1)$$

where T is the absolute temperature, P the pressure, and ΔG, ΔV and ΔH are the specific Gibbs free energy, volume and enthalpy changes, respectively, which is valid for any phase transformation at equilibrium, raises interesting questions about the

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pressure dependence of ΔV and ΔH for starch gelatinisation (Muhr & Blanshard, 1982). ΔV is expected to be very small but (at least for potato starch) positive up to pressures of ~300 MPa when it changes sign, eventually becoming of an appreciable magnitude (but negative) at higher pressures. It is more difficult to conjecture on the pressure dependence of ΔH. The rapid decrease of gelatinisation temperature at higher pressures may be purely a consequence of a large but negative ΔV, but a reduction in ΔH may also play a part. The observed broadening of the gelatinisation range lends some support to a reduction in ΔH as the pressure is increased.

With a view to gaining further insight into these matters it was considered desirable to obtain a more direct measurement either of ΔH or of ΔV as a function of pressure. Fortunately, a high pressure differential thermal analyser (HPDTA) was available to us, and studies using this equipment are reported below.

MATERIALS

The materials used were wheat and potato starch as previously described (Muhr & Blanshard, 1982) and smooth pea starch kindly supplied by Dr D. F. Wright of the Food Research Institute, Norwich. As a standard, HPDTA runs were also made using paraffin wax with a nominal congealing point of 49°C, supplied by BDH Chemicals Ltd.

METHOD

The apparatus has previously been described (Warner, 1975) so only a brief outline is given here. A cross-section of the HPDTA cell is shown in Fig. 1.

The pressure was generated by means of a hand-pump and transmitted to the HPDTA cell via high pressure tubing. The seals between the cell body and the detach-

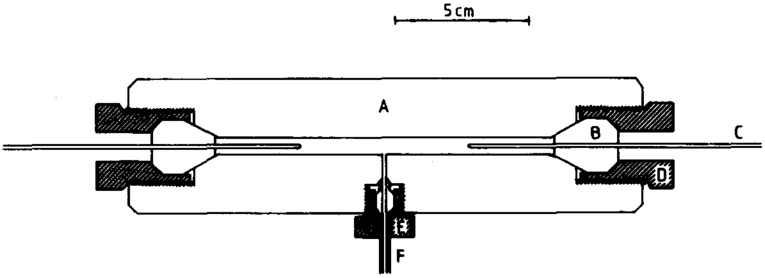

Fig. 1. Cross-section of the HPDTA cell. A, cell body (René 41 alloy); B, conical plugs (René 41 alloy); C, chromel–alumel thermocouple in a stainless steel sheath (diameter not to scale); D, retaining nut (En 56A steel); E, pipe nut; F, high pressure inlet pipe.

able high pressure inlet pipe, and the cell body and the conical plugs (silver soldered on to the thermocouple sheaths), were of the metal-to-metal excess pressure type. Thus for satisfactory sealing at high pressures the three nuts (Fig. 1) had to be tightened very firmly. The pressure medium was Dow Corning silicone fluid 200.

The cell was heated by means of a Thermocoax heating element coiled round (and silver soldered on to) a grooved carbon steel cylinder which was shrunk on to the HPDTA cell body. Steady heating rates were achieved using a Stanton-Redcroft temperature programmer-controller with a 50 ohm platinum resistance sensor mounted longitudinally in one end of the heating jacket. Throughout the course of this study a heating rate of 15°C min^{-1} was used.

The DTA circuit is shown in Fig. 2. The emf corresponding to T (the sample temperature) was fed into the X-amplifier of a Bryans XY chart recorder with a sensitivity of 0·5 mV cm^{-1}, while the emf corresponding to ΔT (the differential temperature) was fed into the Y-amplifier with a sensitivity of 10 μV cm^{-1} for starch or 50 μV cm^{-1} for the paraffin wax comparison runs.

Silica tubes (length 2·5 cm, OD 5·6 mm, ID 3·6 mm) were used for the sample and for the reference. Compacted glass wool (open to the pressure medium) was used as the reference material (Fig. 3). The starch slurry was contained in the tubes by means of blobs of high molecular weight silicone rubber (Fig. 4). As far as possible the sample volume was the same (0·2 cm^3) for each run, as was the position of the sample tube on the probe.

Because the enthalpy change (ΔH) of starch gelatinisation is small, it was necessary to use a sample concentration which would maximise the total ΔH. For this reason a concentration of 1 g air-dry starch to 2 g distilled water was used. At higher concentrations (at least, higher than 1 to 1·55) ΔH on an anhydrous starch basis begins to fall and the peak broadens (Donovan, 1979; Eliasson, 1980; Biliaderis *et al.*, 1980).

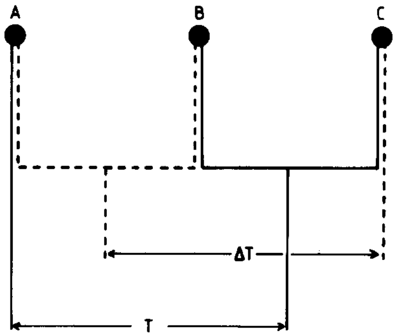

Fig. 2. Circuit diagram for the DTA thermocouples. Solid lines, chromel wires; dotted lines, alumel wires; A, ice/water reference junction; B, junction in the sample; C, junction in the reference.

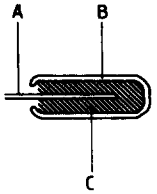

Fig. 3. Arrangement of the reference. A, thermocouple; B, silica tube; C, compacted glass wool, open to the silicone oil.

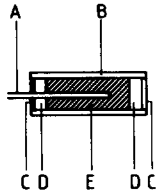

Fig. 4. Arrangement of the sample. A, thermocouple; B, silica tube; C, tinfoil; D, high molecular weight silicone rubber; E, sample.

Before each run the apparatus was cooled to 5°C, using a small quantity of dry ice packed on to the HPDTA cell. The pressure was then raised to the desired level and, after 2 min to allow for temperature equilibration, the run was begun. Stability of the pressure against thermal effects or slow leaks was improved by including in parallel with the HPDTA cell a second pressure cell of large volume.

RESULTS

Paraffin Wax

The performance of the instrument was assessed with a sample of paraffin wax (nominal congealing point 49°C) as a 'standard'. The HPDTA thermograms are shown in Fig. 5. The clearest characteristic temperature of the thermograms is the peak maximum temperature, T_m. A plot of T_m against pressure is given in Fig. 6. The gradient of this plot should be given by the Clapeyron equation (eqn (1)). The slope in Fig. 6 decreases with increases in temperature, whereas for constant ΔV and ΔH the Clapeyron equation requires an increase in slope. It is clear, therefore, that ΔV and/or ΔH change with pressure and temperature. The peak area of the DTA thermograms should be proportional to ΔH. A sample of the same paraffin wax was run on a Perkin-Elmer DSC2 (calibrated with an indium standard) at a heating rate of 10°C

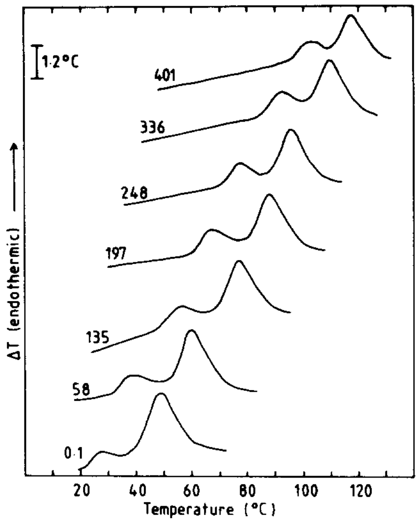

Fig. 5. HPDTA thermograms showing the effect of pressure on the melting peak of paraffin wax. Each thermogram is labelled with the pressure (in MPa) of the run.

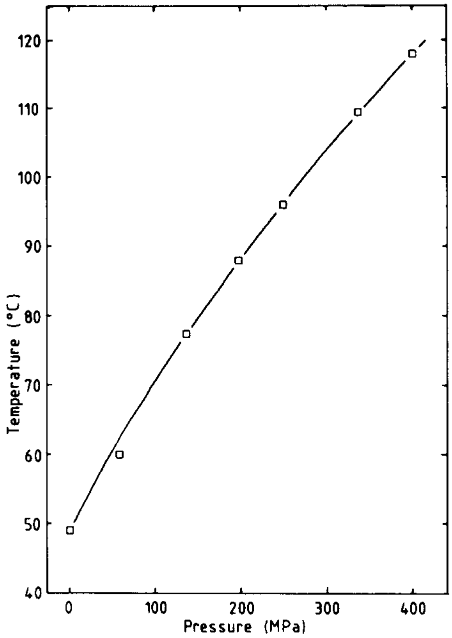

Fig. 6. Pressure dependence of the temperature of the melting peak maximum of paraffin wax.

min^{-1}. A comparison of the DSC thermogram with the HPDTA thermogram is shown in Fig. 7. Measurement of the area under the DSC peak gave a value of 36·1 cal g^{-1} for ΔH, thus giving a conversion factor of 2·15 cal cm^{-2} for HPDTA peaks obtained using the same amplification as in the paraffin wax runs. Using this conversion factor, the values of ΔH along the melting curve have been calculated for the paraffin wax (Table 1). Using these values, and values of dT/dP determined from Fig. 6, the Clapeyron equation yields the values of ΔV (also given in Table 1).

Unfortunately, we have been unable to find data in the literature for a comparable material. However, high pressure dilatometric studies of polyethylene have yielded somewhat similar changes in the thermodynamic data along the melting curve up to a pressure of 160 MPa (Karasz & Jones, 1967; Miyata *et al.*, 1976). From a theoretical point of view, the next best approximation to treating ΔV and ΔH as constant is to treat the heat capacity difference

$$\Delta Cp = Cp_{\text{liquid}} - Cp_{\text{crystalline}} = ((\partial \Delta H)/(\partial T))|_P$$

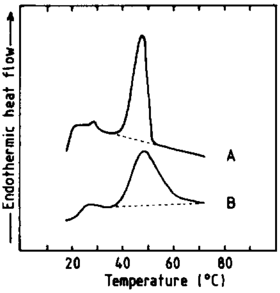

Fig. 7. Comparison of DSC and HPDTA thermograms of paraffin wax at atmospheric pressure. The vertical scales are not equivalent. Dotted lines indicate interpolated baselines used for enthalpy calculations.

TABLE 1
The Effect of Pressure on the DTA Peak Maximum T_m and Thermodynamic Characteristics for Paraffin Wax. ΔV has been Estimated from the other Data using the Clapeyron Equation

Pressure (MPa)	T_m (°C)	ΔH (cal g^{-1})	dT/dP (°C MPa^{-1})	ΔV (mm^3 g^{-1})
0·1	49·4	36·1	0·230	111·4
58	60·0	33·2	0·210	87·6
135	77·5	30·3	0·185	66·9
197	88·1	28·9	0·165	55·3
248	95·9	28·0	0·155	49·2
336	109·6	25·4	0·145	40·3
401	118·0	24·0	0·130	33·4

the compressibility factor

$$\Delta\beta = \beta_{\text{liquid}} - \beta_{\text{crystalline}} = ((\partial \Delta V)/(\partial P))|_T$$

and the thermal expansivity factor

$$\Delta\alpha = \alpha_{\text{liquid}} - \alpha_{\text{crystalline}} = ((\partial \Delta V)/(\partial T))|_P$$

as constants. It is convenient to replace $\Delta H/T$ by ΔS (the specific entropy change) and noting that $((\partial \Delta S)/(\partial P))|_T = -((\partial \Delta V)/(\partial T))|_P = -\Delta\alpha$ we obtain:

$$\left.\frac{\partial T}{\partial P}\right|_{\Delta G=0} = \frac{\Delta V_0 + (T-T_0)\Delta\alpha + (P-P_0)\Delta\beta}{\Delta S_0 + \ln T/T_0 \Delta Cp - (P-P_0)\Delta\alpha} \tag{2}$$

where ΔV_0, ΔS_0 are the values at some P_0, T_0 satisfying $\Delta G = 0$ (see for example Hawley, 1971 and Haynes, 1968). It is therefore only to be expected that ΔV and ΔH (or $T\Delta S$) will change along the melting curve, but once again values for ΔCp, $\Delta\beta$ and $\Delta\alpha$ are hard to find in the literature.

Starch

The HPDTA thermograms obtained for wheat, potato and smooth pea starches are shown in Figs 8, 9 and 10, respectively. It must be remembered that baseline slopes in DTA work are a function of the total heat capacity of the sample versus the reference. The overall slopes of these graphs are thus not of great significance, and the large deviation from the horizontal merely reflects the high sensitivity used. The temperature of the peak maximum, T_m (the easiest characteristic peak temperature to determine) and ΔH (calculated using the areas indicated and the calibration factor determined from the paraffin wax runs, allowing for the five-fold increase in sensitivity, and expressed as cal g^{-1} anhydrous starch) are given in Tables 2-4. Meaningful thermo-

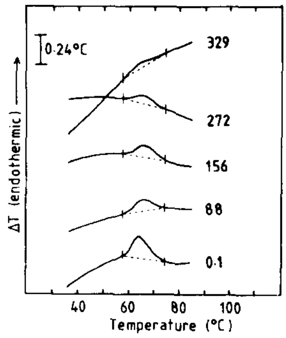

Fig. 8. HPDTA thermograms showing the effect of pressure on the gelatinisation of 33% wheat starch slurries. Each thermogram is labelled with the pressure (in MPa) of the run. Dotted lines indicate the areas for enthalpy calculation.

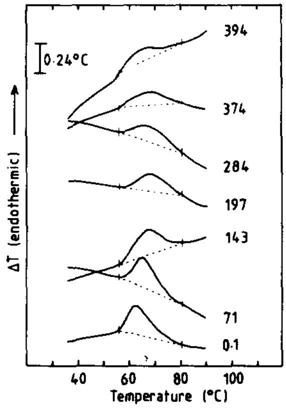

Fig. 9. HPDTA thermograms showing the effect of pressure on the gelatinisation of 33% potato starch slurries. Each thermogram is labelled with the pressure (in MPa) of the run. Dotted lines indicate the areas used for enthalpy calculation.

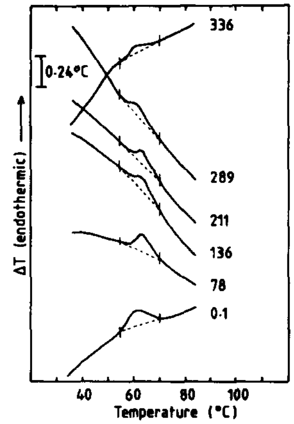

Fig. 10. HPDTA thermograms showing the effect of pressure on the gelatinisation of 33% smooth pea starch slurries. Each thermogram is labelled with the pressure (in MPa) of the run. Dotted lines indicate the areas used for enthalpy calculation.

grams could not be obtained for wheat or smooth pea starches at the highest pressures reported for potato starch because of the indistinct character of the gelatinisation peaks.

While there is a definite decrease of ΔH with pressure for paraffin wax (see Table 1) it is not accompanied by a more diffuse character of the peak, in contrast to the results for starch. We are therefore confident that the values of ΔH given in Tables 1-3

TABLE 2

The Effect of Pressure on the DTA Peak Maximum T_m and Thermodynamic Data for Wheat Starch. ΔV has been Estimated from the other Data using the Clapeyron Equation (Error Arising from Uncertainty in Measuring $dT/dP \pm 0{\cdot}15$ $mm^3\,g^{-1}$)

Pressure (MPa)	T_m *(°C)*	ΔH *(cal g^{-1})*	dT/dP *(°C MPa^{-1})*	ΔV *($mm^3\,g^{-1}$)*
0·1	64·7	3·1	0·027	1·0
88	65·3	2·0	0·009	0·2
143	65·2	1·8	0·000	0·0
156	65·6	1·7	0·000	0·0
272	64·9	1·2	−0·014	−0·2
329	63·2	1·1	−0·039	−0·5

TABLE 3

The Effect of Pressure on the DTA Peak Maximum T_m and Thermodynamic Data for Potato Starch. ΔV has been Estimated from the other Data using the Clapeyron Equation (Error Arising from Uncertainty in Measuring $dT/dP \pm 0{\cdot}3$ $mm^3\,g^{-1}$)

Pressure (MPa)	T_m *(°C)*	ΔH *(cal g^{-1})*	dT/dP *(°C MPa^{-1})*	ΔV *($mm^3\,g^{-1}$)*
0·1	62·4	4·6	0·040	2·3
71	64·6	4·3	0·030	1·6
143	67·3	5·3	0·011	0·7
197	67·6	3·8	0·000	0·0
248	67·2	3·5	−0·010	−0·4
285	66·8	3·4	−0·010	−0·4
374	66·8	3·4	–	–
394	65·6	3·2	−0·017	−0·7

reflect a real effect rather than an artefact of using the apparatus at high pressures. However, the results at atmospheric pressure are rather high compared with 2·3 cal g^{-1} for the same wheat starch and 3·7 cal g^{-1} for the same potato starch using the DSC II directly (Muhr & Blanshard, 1982). The main factor causing this discrepancy is probably the difficulty of interpolating the baseline under the DTA peaks. The important point is that ΔH does decrease with pressure in a fairly consistent manner, and the actual values should not be regarded as definitive determinations.

In contrast to the results for paraffin wax, only small changes in T_m are observed over the pressure range investigated. Since ΔH is small for starch gelatinisation, it is clear that ΔV must be very small and the results are consistent with ΔV becoming zero at about 200 MPa. Using the Clapeyron equation, estimates of ΔV can be made from smoothed T_m versus pressure plots and these are given in Tables 2–4. Direct measurement of such small values of ΔV is difficult but with sufficient care should be possible (see for example Flory & Garrett (1958) who reported a value of 5 $mm^3\,g^{-1}$ for collagen denaturation at atmospheric pressure).

TABLE 4

The Effect of Pressure on the DTA Peak Maximum T_m and Thermodynamic Data for Smooth Pea Starch. ΔV has been Estimated from the other Data using the Clapeyron Equation (Error Arising from Uncertainty in Measuring $dT/dP \pm 0{\cdot}15$ mm^3 g^{-1})

Pressure (MPa)	T_m (°C)	ΔH (cal g^{-1})	dT/dP (°C MPa^{-1})	ΔV (mm^3 g^{-1})
0·1	60·8	2·6	0·030	1·0
78	62·6	1·9	0·010	0·2
136	62·4	1·5	0·000	0·0
211	62·9	0·9	−0·010	−0·1
289	61·2	0·8	−0·017	−0·2
336	60·6	0·8	−0·021	−0·2

DISCUSSION

The results for potato starch are in good agreement with those of Thevelein *et al.* (1981) who found a 4°C rise in the temperature at which 50% of the starch granules (in a 0·4% slurry) lost their birefringence at a pressure of 200 MPa. Muhr & Blanshard (1982) reported a decrease in the temperature at which potato starch granules (in a 12·8% slurry) lost their birefringence at pressures of 450 MPa and above (they gelatinised below room temperature at 800 MPa). Unfortunately, the present pressure rig could not attain such high pressures, but the results do suggest that T_m has reached a maximum at ~200 MPa and has begun to decrease with further increase in pressure.

The only previously published results for the effect of pressure on the gelatinisation of wheat starch are those of Muhr & Blanshard (1982). They reported a small reduction in the temperature at which wheat starch granules (in a 13·3% slurry) lost their birefringence at 200 MPa, a substantial reduction at 300 MPa and at 450 MPa the granules gelatinised below room temperature. However, the reduction at 300 MPa was greater for the first granules to gelatinise (~20°C) than for the last (~8°C). The present results show that for wheat starch as well as for potato starch there is a small rise in gelatinisation temperature up to a pressure of 150 MPa. At first sight the experiments performed at 272 MPa and 329 MPa appear to be in conflict with the results of Muhr & Blanshard (1982). It should, however, be recalled that in these experiments different aspects of gelatinisation were measured, and quite different heating regimes were used (15°C min^{-1} heating rate here, but exposure for 30 min to a predetermined temperature and pressure in the other publication) so that agreement in gelatinisation temperature is not necessary. Nevertheless, the disagreement is puzzling but it is significant that the DTA gelatinisation peak has almost disappeared at 329 MPa and is impossible to locate at higher pressures.

No previous results for the effect of pressure on the gelatinisation of smooth pea starch are available in the literature. It is interesting that pressure has much the same effect as for wheat starch.

According to the Clapeyron equation the approach of ΔH to zero, which is implied by extrapolation of the results presented in this paper to higher pressures, will result in very large values of dT/dP if ΔV is non-zero. Moreover, the results presented here indicate that ΔV is negative at very high pressures, so that they are consistent with the observation of an abrupt fall in gelatinisation temperature at sufficiently high pressures reported in our previous publication (Muhr & Blanshard, 1982). The fact that the fall in ΔH with pressure is considerably more rapid for wheat starch than for potato starch is also consistent with the observation that considerably greater pressures are required to gelatinise potato starch at room temperature than for wheat starch (Muhr & Blanshard, 1982).

Unfortunately DTA is not a suitable technique for investigating the region of low ΔH, as found in this study for wheat and pea starches. Nor can much light be cast on the broadening of the gelatinisation range, which was an interesting phenomenon revealed in our previous publication (Muhr & Blanshard, 1982).

The observed behaviour of a decrease in ΔH with an increase in pressure is probably caused by an increasingly exothermic hydration of the starch molecules, thus tending to annul the (endothermic) heat of fusion of the starch crystallites. Stronger water-starch hydrogen bonds may also be expected to result in a contraction, in agreement with the ΔV values. The reason for the increase in the hydrophilic character of water at large pressures is possibly related to the destruction of water structure, which would result in an increased proportion of open OH groups, and more vigorous solvation of hydrophilic substances. Similar effects of pressure on ΔH and ΔV have been observed for other biopolymers (Hawley, 1971 and Suzuki & Taniguchi, 1972); for a fuller discussion of these points the reader is referred to our previous paper (Muhr & Blanshard, 1982).

CONCLUSION

The initial increase in gelatinisation temperature with pressure, and its subsequent fall, is a consequence of a fall in ΔV from a small positive value at atmospheric pressure to zero at ~200 MPa and finally to negative values at higher pressures. The abrupt nature of the rapid decrease in gelatinisation temperature at high pressures, previously observed for wheat and potato starches (Muhr & Blanshard, 1982), is probably a consequence of the approach of ΔH to zero at these pressures. The changes in ΔV and ΔH, with pressure, point to an increase in the relative strength of starch-water hydrogen bonds as the pressure is increased.

ACKNOWLEDGEMENTS

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