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On the extrapolation of the melting temperature of dry starch from starch–water data using the Flory–Huggins equation

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The experimental results of several workers reported in the scientific literature have been re-analysed using the Flory–Huggins equation. The melting temperatures of various starches were re-calculated from data obtained at different water contents, accepting the possibility of an interaction between the biopolymer and the diluent ($\chi_1 > 0$); the results were compared to those obtained assuming no interaction. The melting temperatures determined by this analysis were between 50 and 100 K higher than those reported in the original papers. © 1998 Published by Elsevier Science Ltd. All rights reserved

INTRODUCTION

The use of the Flory–Huggins (Flory, 1953) equation to describe the dependence of the melting temperature (T_m) of starch on water content was first described by Lelièvre (1974). Some workers, however, consider the use of this equation inappropriate since the melting of partially crystalline polymers such as starch is generally conceived to be a non-equilibrium process (Slade & Levine, 1988). Nevertheless the Flory equation remains valuable as a means of describing the effect of water content on T_m (Lelièvre, 1974; Donovan, 1979; Biliaderis *et al.*, 1980; Biliaderis *et al.*, 1986; Whittam *et al.*, 1991). This approach was further extended by Lelièvre (Lelièvre, 1976) to describe the gelatinization of starch in starch–water–solute systems and used by Blanshard to model the effect of various sugars on the temperature of gelatinization of starch (Blanshard, 1987).

According to this equation the following relation holds between the melting point of a polymer and the diluent concentration:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u}\frac{V_u}{V_1}(v_1 - \chi_1 v_1^2) \qquad (1)$$

where ΔH_u is the change in the enthalpy of fusion per repeating unit (glucose), V_u/V_1 is the ratio of the molar volumes of the repeating unit in the chain to that of water, R is the gas constant, T_m (in K) is the melting point of the polymer–diluent system, T_m^0 is the true melting point of the undiluted polymer, v_1 is the volume fraction of the diluent and χ_1 is an interaction parameter. In an ideal solvent, the interaction parameter χ_1 is nil (Flory, 1953) and consequently a plot of $1/T_m$ against v_1 gives a straight line with $1/T_m^0$ as intercept. Many workers (Donovan, 1979; Biliaderis *et al.*, 1980; Biliaderis *et al.*, 1986) have adopted this simplification when modelling the melting behaviour of starch–water systems.

The aim of this paper is first to demonstrate that such an assumption is inappropriate and second to calculate the 'real' values of T_m^0 and χ_1 from the experimental results of various starches that can be found in the literature.

METHODS

For reasons of clarity, equation 1 was rearranged as follows:

$$f(v_1) = \alpha(v_1 - \chi_1 v_1^2) + \beta \text{ with } \alpha = \frac{R}{\Delta H_u}\frac{V_u}{V_1} \text{ and } \beta = \frac{1}{T_m^0} \qquad (2)$$

The data were acquired by software digitization of the experimental results from the original papers and a non-linear least squares fitting routine was used to optimize the parameters α, β and χ_1, i.e. the minimization of the 'reduced' χ^2:

$$\chi^2 = \frac{\sum^N [f(\upsilon_1) - y(\upsilon_1)]}{N - n} \qquad (3)$$

where N is the number of data points, n is the number of adjustable parameters, $n = 3$ ($N-n$ represents, therefore, the degree of freedom) and $y(\upsilon_1)$ is the experimental value of $1/T_m$ for a particular volume fraction of water, v_1.

The standard errors for each parameter were calculated assuming that the standard error for each datum point is the same and equal to the square root of χ^2.

RESULTS AND DISCUSSION

Figure 1 illustrates the non-linear character of $1/T_m$ versus v_1. It is clear that a linear modelling of such data, even over a limited range as was suggested by Biliaderis *et al.* (1986) would yield an underestimate of T_m^0. The T_m^0 values calculated (Donovan, 1979; Biliaderis *et al.*, 1980; Biliaderis *et al.*, 1986) with the assumption $\chi_1 = 0$ were between 50 and 100 K smaller than those calculated by adjusting χ_1 using the non-linear fitting procedure (Table 1). The fact that these values of T_m^0 are even smaller than the glass transition temperature of starch estimated at 500±10 K by Orford *et al.* (1989) and 516 K by Roos (1995) based on the extrapolation on experimental data reported by other workers (Zeleznak & Hoseney, 1987; Kalichevsky *et al.*, 1992), suggests that they are incorrect.

For all the data analysed, a satisfactory convergence was found for $\alpha = 1.9 \times 10^{-3}$ yielding a value of $\Delta H_u \approx 25.4\,\mathrm{kJ\,mol^{-1}}$, which agrees with the value of $\Delta H_u = 6\,\mathrm{kcal\,mol^{-1}}$ reported by Lelièvre (1976). This value is much smaller than the values of 13.5, 15.8, 16.2 and 18.9 kcal mol^{-1} found for potato (Donovan, 1979), smooth pea (Biliaderis *et al.*, 1980), adzuki bean (Biliaderis *et al.*, 1980) and lentil (Biliaderis *et al.*, 1980), respectively. This difference is probably due to an inappropriate procedure for modelling the data. In the last case, the authors assumed $\chi_1 = 0$ for the calculation of T_m^0 and then used this value of T_m^0 to determine ΔH_u from the intercept of the plot of a rearranged form of the Flory–Huggins equation as a function of v_1/T_m:

$$\left(\frac{1}{T_m} - \frac{1}{T_m^0}\right)/v_1 = \frac{R}{\Delta H_u}\frac{V_u}{V_1}\left(1 - \frac{BV_1}{R}\frac{v_1}{T_m}\right)$$

It was suggested (Lelièvre, 1974) that χ_1 depended on the temperature, $\chi_1 = BV_1/RT$, B being the energy of interaction. Positive B values were reported (Lelièvre,

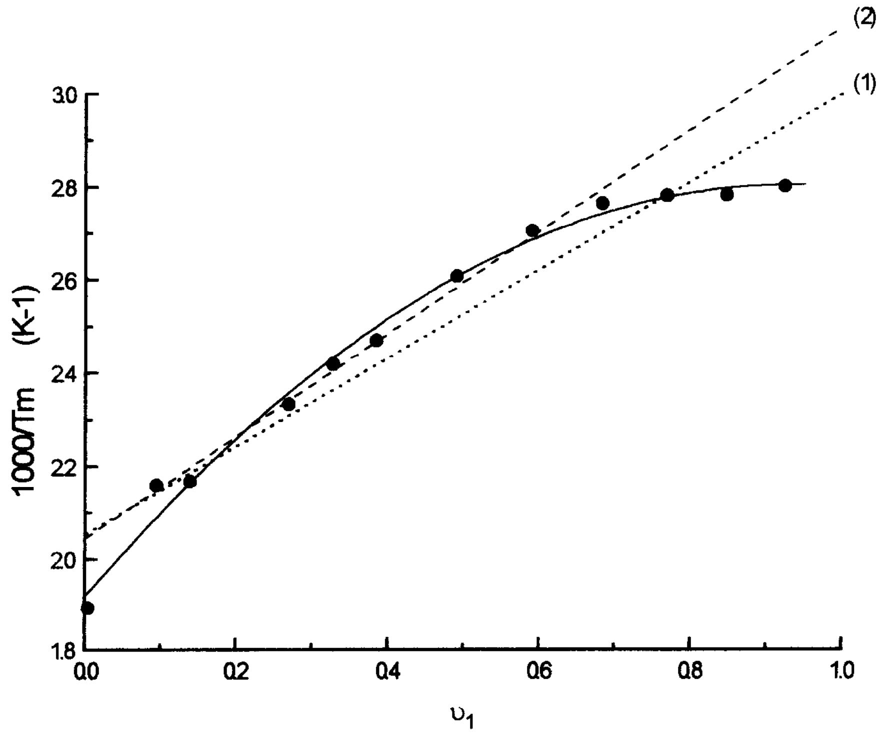

Fig. 1. The plot of $1/T_m$ as a function of the water volume fraction v_1 for rice starch (adapted from Biliaderis *et al.*, 1986). The dotted line (1) shows the linear fit of all the data points while the dashed line (2) represents the linear fit considering the values only of v_1 between 0.1 and 0.7. The solid line (3) shows the non-linear fit of all the data points according to equation 2.

Table 1. The 'true' melting temperature (i.e. in the dry state), T_m^0, of various starches as calculated with $\chi_1 = 0$ and with adjustable χ_1

Sample	Data from reference	Linear ($\chi_1 = 0$) T_m^0 (K)	Non-linear (χ_1 adjustable) T_m^0 (K)	 χ_1
Lentil	Biliaderis *et al.*, 1980	454 (2.1)[b]	525 (4.0)[b]	0.50 (0.016)[b]
Adzuki	Biliaderis *et al.*, 1980	476 (1.3)[b]	571 (3.9)[b]	0.44 (0.013)[b]
Smooth pea	Biliaderis *et al.*, 1980	465 (0.9)[b]	551 (4.4)[b]	0.45 (0.015)[b]
Rice[a]	Biliaderis *et al.*, 1986	476 (5.9)[b, c]490 (3.8)[b, d]	524 (3.9)[b]	0.55 (0.017)[b]
A-type amylose DP15	Whittam *et al.*, 1991	478 (9.6)[b]	523 (5.8)[b]530[e]	0.43 (0.042)[b]0.5[e]

[a]Sample referred to in the original paper (Blanshard, 1987) as RD 4.[b]Values calculated from the experimental results reported by the authors.[c]Obtained from the fitting of all the data points available.[d]Obtained from the fitting of data points for v_1 between 0.1 and 0.7 only.[e]Values reported by the authors.

1974; Donovan, 1979; Biliaderis *et al.*, 1980), leading to positive values of χ_1. This yields, therefore, a contradiction in the modelling procedure.

The values of χ_1 calculated in this paper were found to be 0.5±0.07. This is in agreement with the values suggested by others (Lelièvre, 1976; Blanshard, 1987; Whittam *et al.*, 1991).

CONCLUSION

It has been clearly demonstrated that the dependence of $1/T_m$ on the water volume fraction is better described with $\chi_1 = 0.5$ and that T_m^0 results obtained with the assumption of $\chi_1 = 0$ are undervalued.

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