

STUDIES OF WATER BINDING BY DIFFERENTIAL THERMAL ANALYSIS. II. DOUGH STUDIES USING THE MELTING MODE¹

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ABSTRACT

Cereal Chem. 54(2): 320-325

Melting thermogram differential thermal analysis (DTA) results showed that, up to about 25% moisture content, all the water in dough is of the bound type. Above this moisture content, approximately one-third of the additional water was bound and the remaining two-thirds was free (freezable) water. Doughs from flours (wheat cultivars) of different mixing strength contained

approximately the same amount of bound water. Flour protein content, amount of damaged starch, dough-mixing time, and added chemicals (sodium chloride, N-ethylmaleimide, potassium iodate, ascorbic acid, and cysteine) did not affect the amount of bound water as determined by the melting mode of DTA.

The first article of this series (1) presented results obtained with the boiling mode of differential thermal analysis (DTA). Results by this mode of DTA give a relative measurement of the energy of water binding in dough. This article presents results of a parallel study with the melting mode of DTA. This technique generates data that can be used to calculate the amount of bound and free water in a hydrated biological system such as a flour-water dough.

¹Contribution No. 437 of the Department of Plant Science, The University of Manitoba, Winnipeg, Canada R3T 2N2, with financial assistance from the National Research Council of Canada.

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MATERIALS AND METHODS

Flours

The three flours of different mixing strength used previously (1) were used in this study. The doughs were prepared in the farinograph mixer.

Melting Curve Thermogram

The sample tube containing the dough subsample was weighed and placed in the DTA cell and then frozen at -30°C with liquid nitrogen. Subsequently, the sample was heated to 30°C at a programmed rate of $5^{\circ}\text{C}/\text{min}$ to obtain the endothermic peak at about 0°C due to the uptake of heat by the melting process (Fig. 1). In all experiments, the x- and y-axis sensitivities on the analyzer recorder were set at 10°C (block temperature) and $1^{\circ}\text{C}/\text{in.}$, respectively. Each subsample was frozen only once and three replicate analyses were made for each dough. Endotherm peak areas were determined with a planimeter. The reported results are averages of the three values.

Determination of Bound Water

The amount of free or freezable water was calculated from the melting endotherm peak area according to the procedure described by Davies and Webb (2). The amount of bound water was determined by subtracting the amount of freezable water from the total moisture content of the dough sample. The principle of determining bound water in dough samples using the DTA melting thermogram is based on the fact that bound water is that fraction of the total water (moisture) in the sample that does not freeze at subzero temperatures.

RESULTS AND DISCUSSION

Effect of Mixing Strength and Water Content

Figure 2 shows that with increase in the amount of water in the dough, there is

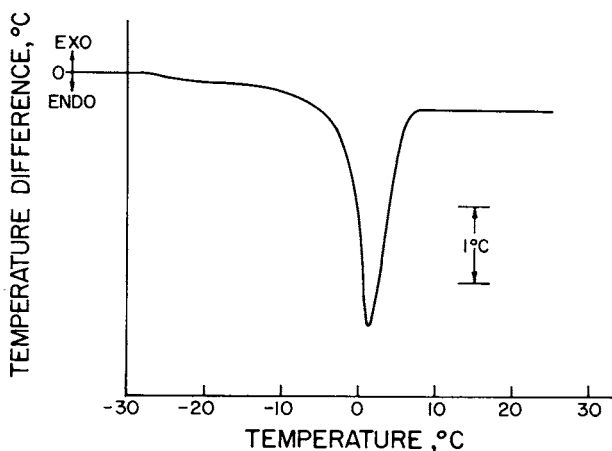


Fig. 1. Typical melting thermogram of a dough containing 46.2% moisture (exo indicates a release of heat and endo absorption of heat).

no freezable water until the dough water content reaches about 0.3 mg/mg (dry flour basis). For higher water contents, free water increases essentially linearly with water content. The points for the three cultivars, which differed markedly in mixing strength, fell essentially on the same curve. That is, dough-mixing strength had no effect on the relation between the amount of freezable water and total moisture in the dough.

According to Fig. 2, the curve intersects the x-axis (dough water content) at a value of about 0.3 mg/mg. Below this moisture level, all of the water is of the bound type. Actually, when the dough containing 24.7% moisture (0.33 mg/mg dry flour) was subjected to DTA it did not show any melting peak, indicating that there was no freezable water in this dough. This amount of bound water is considered to be bound to initially available binding sites on the flour.

If all of the moisture in the dough above 0.3 mg/mg were free water, then the slope of the line in Fig. 2 would be equal to one. However, this is not the case; the actual slope is about 0.65. This indicates that for each g of water added to the dough, only two-thirds is of the free type and the rest is bound water. That is, in the region of water content above 0.3 mg/mg (dry flour basis) the amount of bound water increases linearly with moisture. This increase in bound water with additional moisture suggests that the additional moisture uncovers new sites for water binding that are not accessible initially. Moisture seems to be the key factor in opening up the new binding sites; dough-mixing (at a constant water absorption) does not produce any additional water-binding sites (see below).

In general, the results of the present study agree in two aspects with those of Davies and Webb (2) obtained by differential scanning calorimetry, and disagree in one. The values obtained for the amount of bound water agree reasonably well

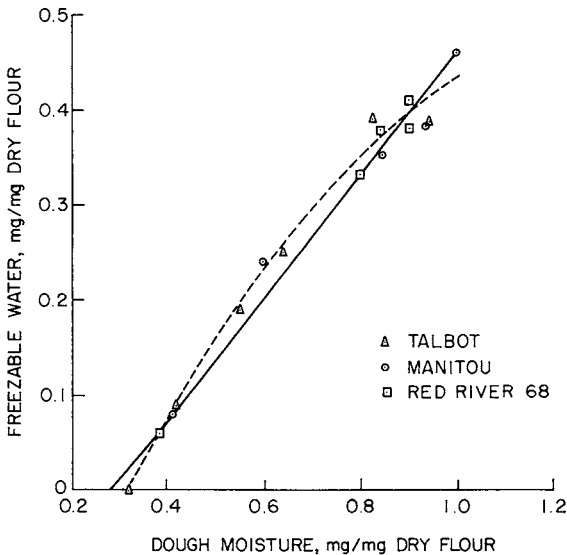


Fig. 2. Effect of moisture content on freezable (free) water of doughs from flours of three different wheat cultivars.

(0.33 mg/mg by Davies and Webb (2) and the minimum value of 0.3 mg/mg from the present study). Davies and Webb (2) found that mixing strength (or baking quality) had no effect on the free-water value; this was also confirmed by the present study.

The two studies disagree on the effect of increasing water content beyond the minimal level obtained by extrapolation on bound water. Davies and Webb (2) reported that all of the water in dough above the minimal value of 0.33 mg/mg was freezable (free) water. In contrast, the present study showed that only about two-thirds of the additional water was of freezable type and the remainder was of the bound type. The explanation for this discrepancy is that the two studies used different modes of thermal analysis. Further research is necessary to clarify this point.

Another way of presenting DTA data on water binding is to plot the amount of bound water against dough moisture. This is obtained by subtracting the freezable water (shown in Fig. 2) from the total moisture in the dough. Figure 3 shows the plot of bound water vs. dough water content obtained in the present study. This presentation of the data gives a curvilinear relationship with the slope increasing as the dough moisture increases. Since the sum of the curves in Figs. 2 and 3 must give a straight line with a slope of one, it might be more accurate to use a curve for the data in Fig. 2 than an approximate straight line.

Effect of Mixing Time

The effect of mixing time was examined for the three wheat cultivars using two

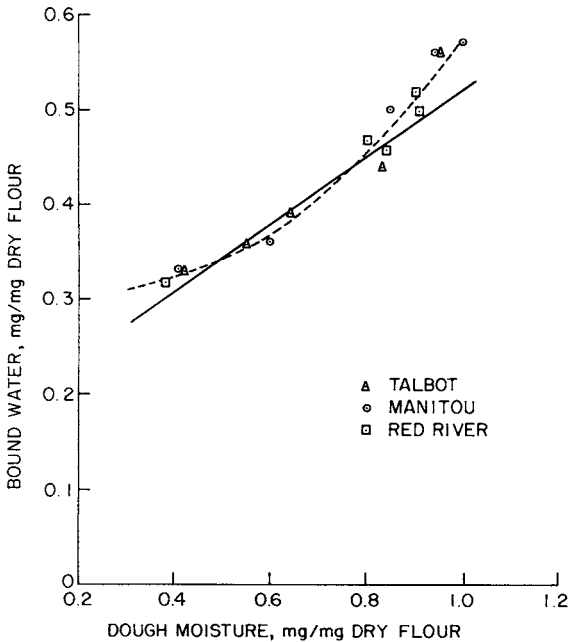


Fig. 3. Effect of moisture content on bound water of doughs from flours of three different wheat cultivars.

different mixing times, 8 min and 20 min. The results obtained (not shown) indicated that mixing time had no effect on the amount of bound water (at the one level of absorption investigated). This result was rather surprising in view of the results obtained by the boiling mode of DTA (1), which showed that mixing had a definite effect on the binding energy of water in dough.

Effect of Flour Protein Content

The effect of protein content on the amount of bound water was examined for one cultivar, Manitou, for which grain samples of different protein content were available and also for all three cultivars where the protein content was increased by adding vital wheat gluten. Protein content had no effect on the amount of bound water in both experiments (Fig. 4). This is rather surprising. It is well known that baking absorption usually increases with protein content. On the basis of results obtained in the present study, it would appear that the higher baking absorption of higher protein content flours results from the requirement of additional free water to maintain the desirable level of dough consistency.

Effect of Starch Damage

The effect of damaged starch was examined using pin-milled flours of the three cultivars. The amount of bound water was not affected by the level of damaged starch (results not shown). Accordingly, it appears that the higher farinograph (or baking) absorption required by flours with higher levels of damaged starch results from the requirement for more water of mobility rather than from an increase in the amount of bound water. The situation with respect to the effect of

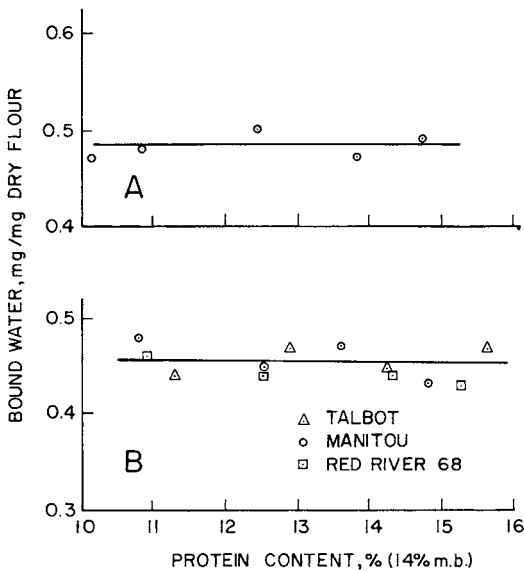


Fig. 4. Effect of protein content on the amount of bound water in dough: (A) flours milled from Manitou samples of different protein content, and (B) flours from three wheat cultivars supplemented with vital gluten.

starch damage appears to be the same as that of increasing protein content described above.

Effects of Salt, Cysteine, N-Ethylmaleimide, and Iodate

For these experiments, doughs containing 2% sodium chloride and 2 $\mu\text{eq/g}$ flour of cysteine, N-ethylmaleimide, potassium iodate, and ascorbic acid were mixed for 20 min at 60% absorption (47.2% water content). The chemicals used had no effect on the amount of bound water as determined by the DTA technique used in this study (results not shown).

GENERAL DISCUSSION

DTA melting mode results showed that all of the water added to dough up to a moisture content of 24.7% (0.3 mg of water/g dry flour) is of the bound type. With further addition of water, the amount of bound water increased by 0.33%/1% of water added. Mixing strength of the flour, protein content, level of starch damage, and addition of chemicals, known to affect the consistency of dough in the farinograph, had no effect on the amount of bound water. Presumably, the variable water that is required to bring a dough to the appropriate consistency (*e.g.*, when different flours are used) for optimal handling in the bakery is free water, or water of mobility, as suggested by Hlynka (3).

Some of the results presented in this article may appear contradictory to the results obtained by the boiling mode of DTA (1). It should be noted that the two modes of DTA measure somewhat different properties. The boiling mode gives a measure of the total energy required to remove bound water and evaporate free water, whereas the melting mode gives a measure of the energy required to melt free (frozen) water only. In other words, the boiling mode can reflect differences in both the intensity and capacity (amount) of water binding, but the melting mode reflects only the water-binding capacity.

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[Received May 11, 1976. Accepted June 17, 1976]