RHEOLOGICAL DOUGH PROPERTIES AS AFFECTED BY ORGANIC ACIDS AND SALT[1]

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ABSTRACT

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Farinograph studies showed that a combination of organic acids isolated from San Francisco sourdough and NaCl profoundly affected dough properties. Mixing time and stability of dough were greatly decreased when organic acids alone were added. Salt had the opposite effect, however, it increased mixing time and dough stability. Combinations of organic acids plus 1.5% NaCl tremendously increased mixing time and dough stability. The original mixing profile of flour could be restored by decreasing the level of NaCl from 1.5 to 1.0%, or by adding 40–80 ppm cysteine-HCl. A hypothesis describing possible changes in gluten structure may explain the action of salt on the behavior of dough at low pH.

Many investigators have studied the separate effects of salts and acids on the physical properties of wheat-flour doughs (1–17). Only two references were found, however, that dealt with the combined effects of acids and salts on dough rheology (18,19). Tanaka et al (18) showed that the farinograph dough consistency of unsalted doughs decreased when the pH was lowered from 5.9 to 4.2 with acetic acid, and that the consistency decreased further when NaCl was present. The combined effects of acetic acid and NaCl, however, were not determined at constant farinograph consistency.

Bennett and Ewart's (19) study indicated that the extensibility of doughs containing both NaCl and acids decreased at low pHs. Acetic and propionic acids, the weakest acids studied, had the least effect on extensibility.

Studies to simulate San Francisco sourdough French bread involve determining the effects of organic acids and salt on dough rheology. Recently, we (20) isolated six organic acids, in addition to acetic and lactic acids, from San Francisco sourdough. Our objective was to determine the effects of NaCl and the combined isolated organic acids on the physical properties of wheat-flour dough.

MATERIALS AND METHODS

Organic Acid Mixture

The organic acid mixture was prepared by transferring the following amounts of organic acids to a 1-L volumetric flask and diluting to volume with distilled water:

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Acid	*Amount (g)*
Lactic	489.0
Acetic	117.0
Propionic	1.83
Isobutyric	0.58
Butyric	0.22
α-Methyl n-butyric	0.13
Isovaleric	0.98
Valeric	0.57

The amounts of organic acids that were used were adjusted to equal the number of the total microequivalents of the acids found in the fully proofed dough (20).

Flour Samples

A commercial hard red winter wheat flour was used throughout the study. The protein and ash contents were 11.31 and 0.43% (14% mb), respectively.

Physical Dough Tests

Farinograph. The AACC official method (21) was used to measure the water absorption of the flour used in the baking tests. The effects of 1.0 and 1.5% NaCl, 40 and 80 ppm cysteine-HCl, 3% sucrose, and organic acids isolated from fully fermented sourdough, added separately, were observed on the general mixing profile of the dough. Different combinations of the substances also were tested. The flour sample size in all cases was 50 g, and the farinograms were determined at constant consistency.

RESULTS AND DISCUSSION

Data on the effects of organic acids, salt, sucrose, and cysteine-HCl on the farinograph curves of the flour used in this study are presented in Table I. The major effects of the additives are discussed below.

Organic Acids

The physical properties of the dough were altered when organic acids were added to the flour-water system in the amounts that were isolated from the fully proofed sourdough. Compared with the no-additive control flour (Fig. 1a), organic acids increased the water absorption by 1% and reduced dough development time by almost 50% (Fig. 1b). Watanabe et al (22) also reported that dough development time decreased as the pH was decreased; they did not keep the dough consistency constant, however, so the effect of acid on flour absorption could not be determined.

When the concentration of the added acids was held constant, organic acids had a slightly greater effect on decreasing the peak time and altering the general characteristics of the farinogram than did acetic acid. These results were expected, since the pK_a of the acetic acid (4.74) was higher than that of the lactic acid ($pK_a \sim 3.86$), which constituted more than two-thirds of the organic acid mixture. When the acetic, lactic, and isolated organic acids were added at a constant concentration (74.33 μeq/g of dough), the dough pHs were 4.20, 3.70, and 3.82, respectively. Therefore, the results suggested that the pH had a greater effect on the physical dough characteristics than did the conjugate base.

Though controversies exist in the literature on the effects of acid on the farinograms of dough, gluten is generally believed to be broken down by acid, ie, low pH (18). The reduced dough stability and increased tolerance index observed in this study when organic acids were added to the flour (Table I) lend credence to that theory.

The mechanism by which acid disrupts the gluten structure is uncertain. The breakdown of the protein has been postulated to be caused by the cleavage of the protein salt linkages by the action of either the hydrogen ion or the anionic acid residue (18,19).

Salt

Adding salt to the flour markedly affected the physical characteristics of the dough, especially when 1.5% was used. Two notable effects of this salt level were a 1.4% decrease in water absorption and a 2-min increase in development time of dough (Fig. 1c). These data substantiate Hlynka's work (8).

The effect of salt is thought to be primarily due to changes in gluten hydration, a phenomenon Bushuk and Hlynka (23) explained by using the concepts of "free" and "bound" water. When salt is present in a dough system, it is thought to increase the amount of free or mobile water in the system by altering the gluten structure in such a way that the salt occupies the sites once occupied by the bound water. This theory helps to explain why water absorption decreases when salt is added and dough consistency is held constant, and the toughening or

TABLE I
Effects of Organic Acids, Salt, Sugar and Cysteine-HCL on Flour Farinogram Values

Additive	Water Absorption[a] (%)	Arrival Time[b] (min)	Peak Time[c] (min)	Stability[d] (min)	Tolerance Index[e] (BU)
Control (no additive)	63.6	1.7	8.7	13.5	20
Organic acids[f]	64.6	1.4	4.5	4.0	150
1.5% NaCl[g]	62.2	2.5	10.7	23.5	15
3% Sucrose[g]	63.6	2.0	9.0	12.0	40
Organic acids plus 1.5% NaCl	58.0	1.5	17.0	28.0	25
Organic acids plus 1.0% NaCl	58.8	1.0	9.5	18.0	15
Organic acids plus 1.5% NaCl plus 3% sucrose	58.0	1.7	17.3	24.3	35
Organic acids plus 1.5% NaCl plus 40 ppm cysteine-HCl[g]	57.8	0.7	10.2	18.5	30
Organic acids plus 1.5% NaCl plus 80 ppm cysteine-HCl[g]	57.4	1.0	8.5	13.8	40
Organic acids plus 1.0% NaCl plus 40 ppm cysteine-HCl[g]	58.5	1.0	8.2	13.0	30

[a] Amount of H_2O required by given weight of flour to yield dough consistency of 500 BU.

[b] Time to reach 500-BU line.

[c] Time required for dough to reach maximum development.

[d] Difference between arrival time and time it takes for curve to decrease below 500-BU line.

[e] Difference in BU units from top of curve at peak to top of curve measured 5 min after peak. This is an inverse relationship, ie, the higher the value, the lower the tolerance to mixing.

[f] Mixture of organic acids was added according to amounts found in fully proofed sourdough (see methods).

[g] Flour basis.

strengthening effects of salt, which result in longer dough development times.

Among other major effects, when 1.5% salt was added to flour, the rate of water absorption by the flour decreased, ie, arrival time and dough stability increased. Changes in both of these parameters may be explained by considering the effects of salt on gluten hydration described in the previous paragraph.

Sucrose

Sucrose added at the 3.0% level did not significantly change any of the parameters of the control curve except for the stability and the tolerance index (Table I). In that instance, sugar caused the stability to decrease by 1.5 min and the tolerance index to double, indicating that this dough was less tolerant to

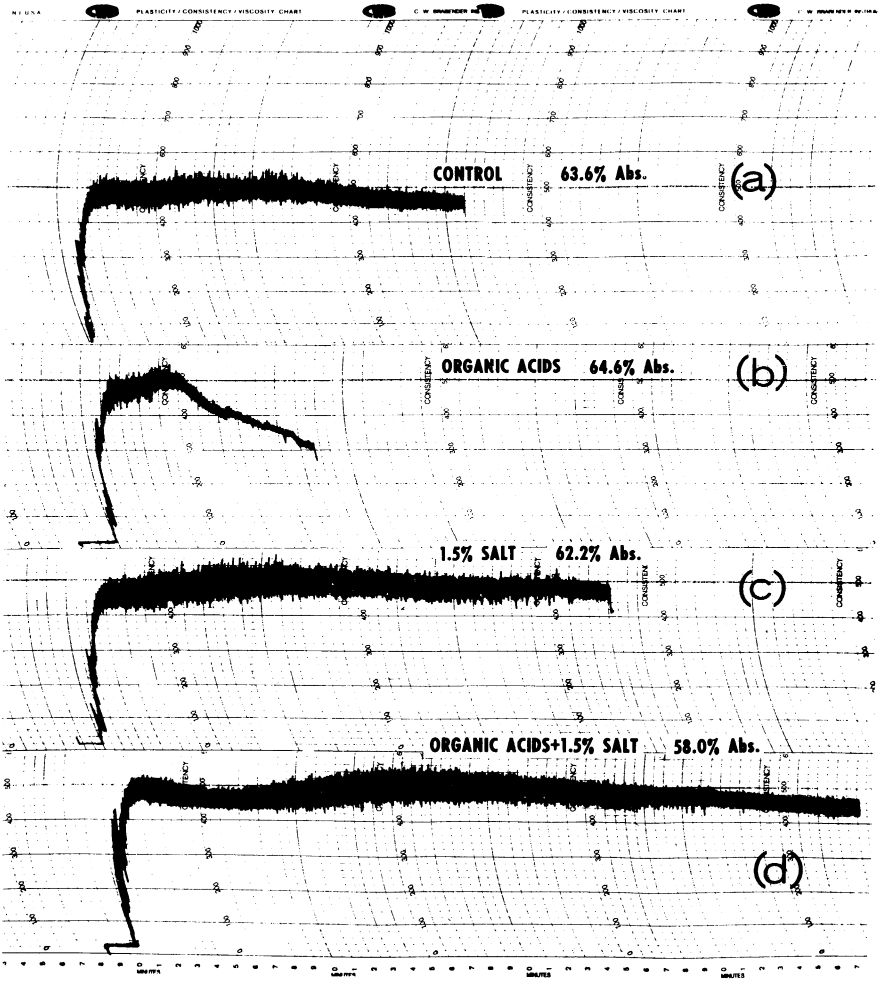

Fig. 1. Farinograms showing control ADM flour (a) and effects of organic acids (b), 1.5% NaCl (c), and organic acids plus NaCl (d) on physical characteristics of control flour.

mixing than was the control. Likewise, Bohn (24) showed that 3% sucrose had little effect on physical dough characteristics. We do not know, however, why stability and mixing tolerance decreased. Bohn (24) suggested that sugar has a "softening" effect on gluten, but he did not postulate any mechanism of action.

Organic Acids Plus Salt

The effects produced by incorporating both organic acids and salt into the flour varied with the factor measured or the levels of salt that were added or both. For example, compared with the control, the water absorption of the flour decreased substantially when organic acids plus salt were added to the flour; this was true regardless of the level of salt (1.5 or 1.0%) (Table I). When 1.5% NaCl was added, however, water absorption was lower (5.6%) than when 1.0% salt was added (4.8%). These findings were unexpected, because when these substances were used alone, the organic acids increased absorption and the salt decreased absorption.

The combination of organic acids plus salt also increased dough-development time and dough stability (Fig. 1d). The absolute effects, however, varied with the level of salt combined with the organic acids, ie, adding 1.5% salt produced a greater increase in the two factors than did adding 1.0% salt. In the presence of organic acids, 1.5% salt increased the mixing time by 8.3 min compared with only 0.8 min when 1.0% salt was added (Table I). Therefore, reducing the salt content by 0.5% is apparently quite critical in determining the mixing time when organic acids are present in the dough.

What chemical reactions occur when acids and salt are combined in a dough system are not known exactly. Possible reactions when organic acids plus NaCl are added are discussed below.

The gluten proteins, which play a large role in determining the physical characteristics of the dough and in water absorption, have an isoelectric point ranging from pH 6 to pH 9 (25,26). Lowering the pH to 3.8 or 3.9 will result in a net positive charge on the proteins due to the protonation of some of the carboxyl anions of glutamic and aspartic acids, which have a pK_a of about 4.6. This net positive charge causes intramolecular and intermolecular repulsions to increase.

Intramolecular repulsions cause the flexibly coiled part of the protein molecule to uncoil or unfold, producing a somewhat open structure. The resulting conformational changes could increase the water-binding capacity of the protein, because more positively charged groups are available to interact with water. Also, the repulsion of the like charges would create more space for entrapping more water. On the other hand, some hydrophobic groups also may be exposed so that possible intermolecular hydrophobic interactions could occur, which would agglomerate the protein molecules. Electrostatic repulsive forces, however, are much stronger than are short-range forces holding nonpolar molecules together. Therefore, interactions between the positively charged repulsive groups and water probably would be the most dominant effect occurring.

Wehrli and Pomeranz (27) have suggested that salt, which masks the repelling action of molecular charges, suppresses the intermolecular repulsions to a greater extent than the intramolecular repulsions. Therefore, what needs to be determined is the effect this repelling action might have on a dough system.

The amino acid composition of gluten shows that about 8% of the total amino acid residues are ionizable (28). These ionic residues are distributed between acidic (3.2%) and basic (4.8%) amino acid residues (a ratio of 2:3). Most acidic residues consist of glutamic acid, which has a pK_a of about 4.6; few aspartic acid residues are present. The basic amino acid residues, however, are distributed among arginine (about 2.2%), histidine (about 1.5%), and lysine (about 1.1%). The total polar (hydroxyl plus amide) and the total nonpolar amino acids represent about 40 and 38%, respectively, of the total amino acid residues (28). Therefore, we might predict that around pH 5.5, the average pH of conventional white bread, the gluten proteins would have a small net positive charge. Under those conditions, lysine (ϵ-amino $pK_a \sim 10$) and arginine (quanido $pK_2 \sim 12.5$) would be entirely in the positively charged form, while glutamic and aspartic acids would be essentially in the negatively charged form. Histidine (imidazole $pK_a \sim 6.3$) would be about half protonated. Adding salt to this bread dough (pH 5.5–6.0), would appreciably decrease the intermolecular and intramolecular repulsions by interacting with the charged groups on the protein molecules. In turn, the interactions of the salt ions with the protein would decrease the amount of water that could be bound by the gluten, ie, water absorption would be decreased. Therefore, adding salt might produce a slightly more folded conformation of the protein molecules and more compact protein aggregates.

A much different effect on the protein structure undoubtedly results when salt and acid are both present in the dough. The acid would lower the pH and therefore increase the repulsive forces between the positively like-charged side chains, causing the coiled part of the molecule to unfold. On the other hand, salt would suppress the intermolecular repulsions, particularly in the unfolded part of the protein molecules, and in so doing would lower water absorption by tightening and aggregating the protein molecules. Salt would enhance protein aggregation, but could not reverse the changes in conformation caused by the low pH.

As described above, acid would increase the number of positively charged sites available for interactions with salt ions, as well as exposing more hydrophobic groups. In addition, because salt would suppress the intermolecular ionic repulsions, the exposed hydrophobic groups would be freed to interact, and that in turn would result in a further strengthening of the protein structure. (Such a great hydrophobic interaction would not exist if acid or salt were present separately.) Eventually, the extremely insoluble protein would increase the tendency to form compact aggregates. These reactions would explain the synergistic effects we observed in this study when organic acids and salt were combined. Also, the findings of some authors (28) that insoluble proteins impart strength to wheat flour doughs whereas more soluble proteins have a weakening effect further supports this interpretation. The proposed theory is summarized in Fig. 2.

Adding Cysteine-HCl

Cysteine-HCl, 40 and 80 ppm (flour basis), was used in an attempt to restore the peak time of the organic acids-plus-salt system back to the peak time of the normal no-additive control. As can be seen from Table I, the peak time of the acids-plus-1.5% salt system was reduced by 6.8 min when 40 ppm cysteine-HCl was added. When 80 ppm cysteine-HCl was added, the differences between the peak times of the acids-plus-salt system and the control were insignificant. Both levels of cysteine, however, slightly decreased the water absorption of the acids-plus-salt mixture. The greatest decrease was 0.6% when 80 ppm cysteine-HCl was used in the presence of organic acids plus 1.5% salt.

The peak time of the acids-plus-salt system was also restored when 40 ppm cysteine-HCl and 1.0% salt were used. In this instance, a slight increase (0.5%) in water absorption was observed.

The effects of cysteine on the acids-plus-salt dough system generally agreed with earlier reports, which indicated that cysteine decreased dough mixing time (29). Tsen (29) has postulated that cysteine reduces the mixing time, because it

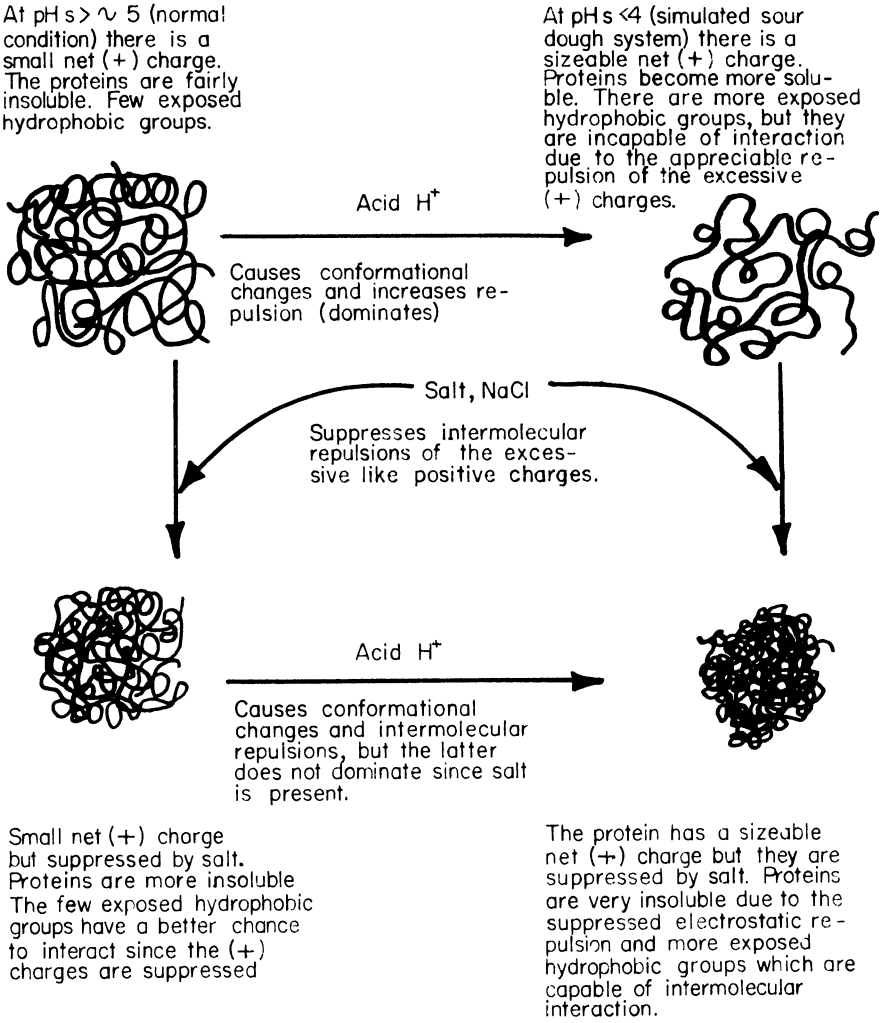

Fig. 2. Schematic diagram showing possible effects of pH and salt on wheat gluten proteins.

promotes sulfhydryl-disulfide interchange reactions that accelerate dough development.

Henika and Rodgers (30) and Chamberlain et al (31) have shown that the response to added cysteine is influenced by the strength of the flour. Strong flours respond more readily than do weak flours, which might help to explain why dough containing acids plus 1.5% salt responded to a much greater extent when cysteine was added than did dough containing acids plus 1.0% salt. The small increase in the salt level (from 1.0 to 1.5%) seemed critical and might have strengthened the gluten enough to give the flour some of the characteristics typical of a strong flour, so that the response of a 1.5% dough to cysteine was much greater than that of a 1.0% salt dough.

Organic Acids Plus Salt Plus Sucrose

The effects of sugar on the acids-salt system were, in general, similar to those produced by the acids-plus-salt system alone (Table I). Adding sugar, however, decreased dough stability and increased the tolerance index, changes that might have been related to the "softening" effects of sugar on gluten (24).

SUMMARY

The effects of acids, salt, and a combination of both on physical dough properties were studied. Adding organic acids substantially decreased mixing time and weakened the dough; NaCl increased the mixing time and strengthened the dough. A combination of both acids and salt increased mixing time and greatly increased dough strength, probably because of changes in gluten protein conformation. After many mixing trials, adding cysteine-HCl or 1.0% instead of 1.5% NaCl in the presence of organic acids was found to restore the mixing profile of the original flour.

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