

Chemical Leavening: Effect of pH and Certain Ions on Breadmaking Properties¹

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ABSTRACT

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When a combination of yeast and chemical leavening was used in bread, yeast was tolerant to moderate changes in pH but its gassing abilities were impaired when subjected to high pH (≥ 9.7). At the pH encountered in doughs containing NaHCO (~ 6.75), the yeast was about 90% as active as control dough (pH 5.5). A laboratory-scale, remixing scheme was developed to incorporate chemical leavening into yeasted doughs. Baking

results indicated that the major factor affecting loaf volume was not pH, but rather the salts produced from the leavening reaction. Specific ions were detrimental to loaf volume. A mixograph study characterized the effect of ions on the mixing curve, and results corresponded to the anionic lyotropic series. A baking study of selected ions of the anionic lyotropic series supported the mixograph results.

The word "leavening" is derived from the Latin *levare* "to raise" and means raising or making light (Kichline and Conn 1970). The use of chemical reactions for leavening was patented in 1838 in England (Conn 1981). Carbon dioxide (CO₂) is the principal leavening gas and is produced by one of three mechanisms: fermentation, where yeast ferments sugar and produces alcohol and carbon dioxide; decomposition, where ammonium bicarbonate in the presence of heat produces ammonia, water, and carbon dioxide; and the reaction of an acidic salt and sodium bicarbonate in the presence of moisture and heat to form a salt, water, and carbon dioxide. The third mechanism is popular because of sodium bicarbonate's low cost, lack of toxicity, ease of handling, tasteless end products, and high purity (Conn 1965).

Because soda dissolves almost immediately, the leavening acid's rate of dissolution, which in turn depends on the available water, determines the rate of CO₂ release. Leavening acids, therefore, are characterized by leavening rates. There are two broad classifications of leavening rates. Fast-acting acids liberate as much as 80% of the leavening gas during mixing and standing (Anonymous 1983). An example of a fast-acting acid is monocalcium phosphate (MCP). MCP's leavening reaction produces most of its gas within 2 min after mixing. There is virtually no gas produced on standing. The remaining gas is evolved during baking. The other type, slow acting, produces the major portion of CO₂ as the temperature of the product rises during baking (Anonymous 1983). An example of a slow-acting acid is sodium aluminum phosphate (SALP). SALP has a relatively slow reaction rate during mixing and minimal CO₂ production during standing. Maximum reaction potential is retained for baking. Other examples of fast- and slow-acting acids are described by Conn (1965, 1981) and LaBaw (1982).

Neutralizing Value

The concept of neutralizing value was developed to compare the available acidity (CO₂-releasing power) of various leaveners and, more important, to calculate the correct level of usage (Conn 1965, 1981; Kichline and Conn 1970). Neutralization value is defined as the parts by weight of sodium bicarbonate that will neutralize 100 parts by weight of an acid leavener so as to convert the bicarbonate to carbon dioxide.

Effect of Salts on Dough Rheology.

Salovaara (1982) reported that the effect of electrolytes on dough rheology is based on gluten protein aggregation. Similar

results were reported many years earlier (Smith and Bailey 1923). Theoretically, ions may enhance either protein association or dissociation. The stabilizing effect of sulfate on a native configuration of protein compared to that of chloride is a well-known phenomenon (von Hippel and Wong 1964). The strengthening effect of sodium sulfate on wheat dough compared to sodium chloride also has been reported (Guy et al 1967). Furthermore, Evans et al (1975) stated that phosphates cause the protein matrix in spaghetti to retract, which inhibits the development of a cohesive continuous matrix.

The purpose of this study was to determine if a combination of yeast and chemical leavening or chemical leavening alone would be beneficial in bread doughs. Because chemical leavening agents affect both pH and the salts in dough, both of those factors were studied.

MATERIALS AND METHODS

Ingredients

Two shipments of a commercial bread flour (flours A and B) from Ross Mills, Wichita, KS, were used in preparing bread doughs. Flour A contained 12.3% protein and 0.47% ash. Flour B contained 11.9% protein and 0.46% ash. Hydrogenated vegetable shortening (Crisco, Proctor & Gamble, Cincinnati, OH) was also used in the bread formula. Fermipan instant dry yeast (Gist-brocades, Delft, The Netherlands) was used.

Sodium bicarbonate was obtained from the Church & Dwight Co., Princeton, NJ. The leavening acids were acquired from Stauffer Chemical Co., Westport, CT, except for sodium aluminum sulfate, which was obtained from Allied Chemical, Morristown, NJ. The sodium and chloride salts of the cationic and anionic lyotropic series were purchased from Fisher Scientific Co., Fair Lawn, NJ. All chemicals were reagent grade.

Straight-Dough Method

Doughs for baking experiments were prepared using the straight-dough procedure described by Finney (1984). Doughs were mixed to optimum in a National 100-g pin mixer (National Mfg. Co., Lincoln, NE) and fermented at 30°C, 90-95% rh, in a proof cabinet (National Mfg.). A 180-min fermentation time was used with mechanical punches at 105- and 155-min intervals. At the end of the fermentation, the dough was sheeted through rolls set at 5/16-in. opening and molded with a drum molder (Thomson Co., Belleville, NJ). The molded dough was panned and proofed at 30°C, 90-95% rh, for 55 min and baked at 218°C for 24 min. The weight and volume of the loaf were measured immediately after baking. Volume was determined by rapeseed displacement.

pH Determination

To determine the pH of dough, a 10-g sample was added to 100 ml of distilled water. The sample was then blended for 1 min at high speed in a blender. A Corning model 125 pH meter with electrodes

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that had been calibrated against known buffer solutions was used to determine hydrogen-ion activity. The sample was continuously agitated and a reading taken when the meter stabilized. Hydrogen-ion activity of bread samples was determined by using AACC method 02-52 (AACC 1976).

Mixograph

A National Mfg. 10-g mixograph, described by Finney and Shogren (1972), was used to study the effects of various ions on mixograph curves. Flour (10 g, weighed on 14% moisture basis) was placed in the mixograph bowl. An optimum water absorption (58%) was determined for the control (flour and water). Various dilutions of different molar solutions of selected sodium salts of the anionic lyotropic series, citrate > tartrate > sulfate > acetate > chloride > nitrate > bromide > iodide > thiocyanate (Bull 1964)—and selected chloride salts of the cationic lyotropic series—thorium > aluminum > hydrogen > barium > strontium > calcium > potassium > sodium > lithium (Bull 1964)—were added to bring the flour sample to the optimum 58% water absorption. Each sample was mixed for 8 min. An example of the effect of different

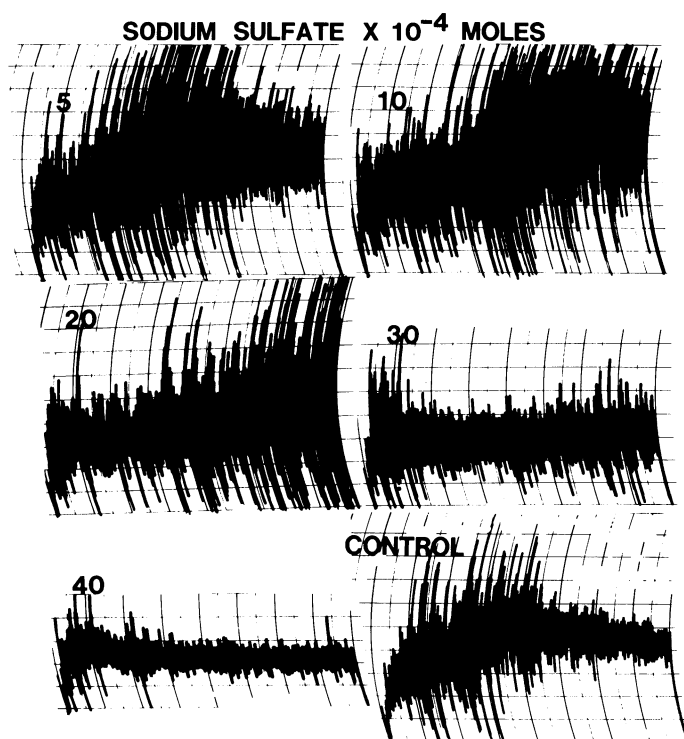


Fig. 1. Mixograms of the salt concentration series for sodium sulfate.

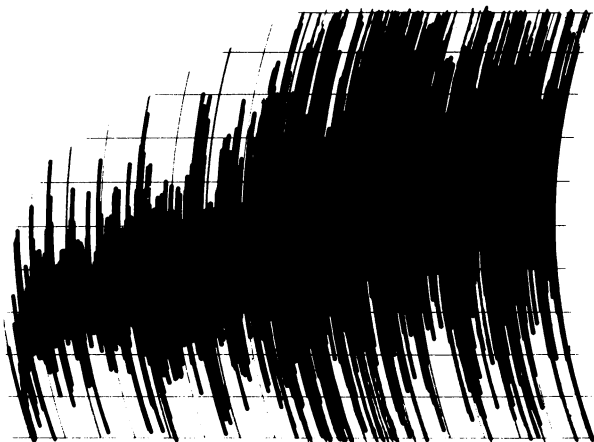


Fig. 2. Specified curve type for mixograph study on lyotropic ion series.

sodium sulfate concentrations on mixing curves is shown in Figure 1. A similar series was produced for the other salts. A specific curve type (Fig. 2) was identified from each of these salt series, and the grams and moles of salt needed to produce the curve type were determined. This allowed comparison of the effects of the different salts.

Gassing Power Determination.

The gasograph (DSI Gasograph 12) was used in all determinations of gassing power (Rubenthaler et al 1980). A 15-g sample of dough was placed in a gasograph vessel. The vessel was then placed in a 30°C water bath and allowed to stand 2 min before connecting the gas tube to the reaction vessel. This time interval allowed for thermal expansion of the air in the reaction vessel, which should not be considered as part of the total volume of evolved gas. Each sample was prepared as above and placed on the gasograph at regular intervals. Gas production in gasograph units (GU) was determined over 3 hr of fermentation time.

Remix Procedure

The scheme for remixing to incorporate the chemical leavening into the dough is shown in Figure 3. Doughs were mixed to optimum development in a National 100-g pin mixer and fermented for 60 min at 30°C, 90–95% rh, in a proof cabinet. These doughs were then remix for 1½ min to incorporate the acid and soda and fermented at 30°C, 90–95% rh, for another 30 min to relax the dough. The optimum relaxation and remix times were determined to achieve uniform incorporation of the leaveners without overmixing. At the end of the relaxation time, doughs were processed as outlined above. Doughs were subsampled (10 g) for pH determinations, and the loaf volumes were normalized to bring the values into conformity with the 100 g standard flour basis.

Preparation of Chemical Leavening and Reaction Salts

Various amounts of soda were weighed. Acid was added in sufficient amounts to neutralize the soda. The following equation

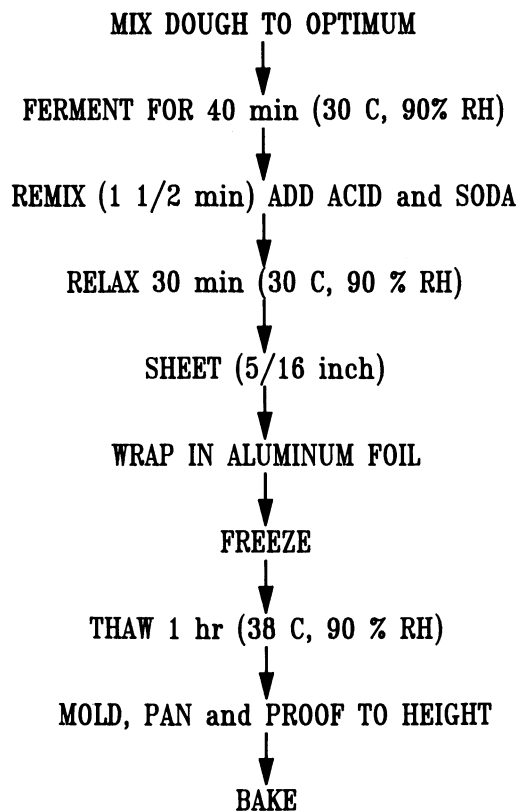


Fig. 3. Scheme for remix procedure.

was used in the calculations:

$$\text{Acid (g)} = \frac{\text{Soda (g)}}{\text{Neutralization Value}} \times 100$$

Specific neutralization values for the various leavening acids were supplied by the manufacturer.

The reaction salts from the above combinations were produced by adding a small volume of distilled water to the acid and soda. The sample was then heated and allowed to boil for approximately 1 min. The salts produced from the reaction were added as part of the water when the dough was mixed.

RESULTS AND DISCUSSION

Effect of pH on Gas Production

Preliminary work was designed to study the combination of yeast and chemical leavening agents in bread doughs. The optimum pH for yeast activity (gas production) is known to be approximately 5.5 (Pylar 1973). However, it was not clear from the literature how tolerant yeast was to changes in pH. Therefore, gas production was determined as a function of pH (Fig. 4). The figure shows that yeast was relatively tolerant to changes in pH, with a substantial rate of gas production (80% of optimum or better) between pH 3.7 and pH 8.0.

These results were encouraging. If yeast had been more sensitive to pH, then the possibility of using combinations of yeast and chemical leavening would be remote. The fact that we could obtain substantial gas production at alkaline pH was particularly critical because sodium bicarbonate (NaHCO_3) would adjust the dough pH into this range.

The effect of higher pH values on yeast was also studied. It was not known if the yeast is killed by higher pH or if it becomes dormant and can become active again if the pH is readjusted to a more favorable range. To investigate this phenomenon, a dough was adjusted to pH 9.7 with sodium carbonate. At that pH the yeast produced very little gas. After exposure to pH 9.7 for 5 min, the pH was adjusted to 5.7 with lactic acid. The gassing rate (17.5 GU/3 hr) was much lower than that for the control unadjusted dough (pH 6.1 and 27 GU/3 hr). It was concluded that when yeast is subjected to high pH (≥ 9.7), its gas producing ability is permanently impaired.

Effect of pH on Loaf Volume

Although it was clear that substantial gas production was obtained over a wide range of pH values, the question of what type of bread would be produced at the various pH values was still unanswered. Therefore, doughs were prepared at five pHs: 4.65 and 5.30 (lactic acid), 6.15 (control), and 6.86 and 7.72 (NaHCO_3). Mixing time for the doughs varied with pH. All doughs were proofed to a constant height and baked. Loaf volume was affected

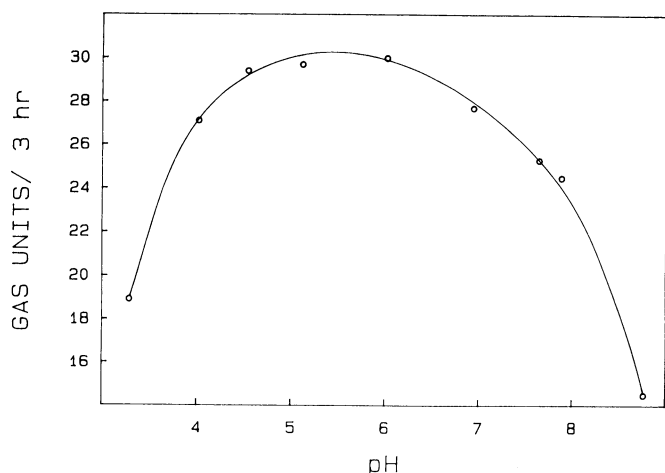


Fig. 4. Effect of pH on yeast activity.

by the dough pH, as were the texture and crumb grain of the bread (Table I). In these experiments, no leavening acid was used. Therefore, the only gas produced was from the yeast and thermal decomposition of the NaHCO_3 .

Effect of Leavening Acids on Loaf Volume

The feasibility of remixing dough as a way to incorporate the leavening acids and soda into the dough was studied using a control dough and a remixed dough (processed as outlined in Fig. 1 without adding acid and soda). The results showed that the loaves were comparable and that remixing was not detrimental to loaf volume.

Although it was clear that remixing dough was feasible, the effect of chemical leaveners on dough still had to be established. Doughs were prepared with two leavening acids. The first, SALP, is slow acting and triggered by heat. The second acid, MCP, is a fast-acting acid that will dissolve at room temperature. Loaf volumes were decreased by the addition of both leavening acids (Table II). This was an unexpected result, because the additional CO_2 supplied by chemical leaveners was expected to boost the loaf volume.

Doughs were prepared with various ratios of soda to acid in order to vary the pH during mixing, fermentation, and baking. The goal was to produce a pH immediately before baking comparable to the control pH at the same step. However, even with the adjustment in pH, the volume was much lower than that of the control (Table III). In fact, when additional leavening acid was

TABLE I
Baking Results (Flour A) at Varied Dough pH Values

| Dough pH | Mixing Time (min) | Proof Time (min) | Loaf Volume (cm^3) | Crumb Grain |
|----------------|-------------------|------------------|-------------------------------|----------------|
| 4.65 | 3½ | 60 ± 3 | 742 ± 10 | Tight |
| 5.30 | 3½ | 58 ± 2 | 860 ± 5 | Slightly tight |
| 6.15 (control) | 3½ | 55 ± 0 | 938 ± 21 | Normal |
| 6.86 | 4 | 69 ± 2 | 905 ± 30 | Slightly open |
| 7.72 | 5½ | 75 ± 4 | 816 ± 20 | Open |

TABLE II
Effect of Chemical Leavening on Dough pH and Bread (Flour A)

| Sample | pH After Mix | pH After Remix | pH of Baked Loaf | Loaf Volume ^a (cm^3) |
|--------------------------------------|--------------|----------------|------------------|--|
| Control | 6.02 | 5.60 | 5.51 | 1,025 ± 15 |
| Remixed | 6.08 | 5.62 | 5.50 | 1,038 ± 21 |
| SALP ^b + soda (1 g:1 g) | 6.13 | 7.01 | 7.04 | 798 ± 18 |
| MCP ^c + soda (1.25 g:1 g) | 6.00 | 6.71 | 6.83 | 831 ± 19 |

^aNormalized to 100 g of flour.

^bSALP = Sodium aluminum phosphate.

^cMCP = Monocalcium phosphate.

TABLE III
Effect of Leavening Acids on Loaf Volume (Flour A)

| Sample | pH After Mix | pH After Remix | pH Before Oven | pH of Baked Loaf | Loaf Volume ^a (cm^3) |
|--------------------------------------|--------------|----------------|----------------|------------------|--|
| Control | 6.01 | 5.56 | 5.33 | 5.56 | 1,064 ± 10 |
| Remixed | 5.97 | 5.50 | 5.29 | 5.57 | 1,043 ± 12 |
| SALP ^b + soda (1 g:1 g) | 5.99 | 6.76 | 6.73 | 6.81 | 893 ± 16 |
| MCP ^c + soda (1.25 g:1 g) | 5.95 | 6.68 | 6.56 | 6.81 | 857 ± 21 |
| (2.25 g:1 g) | 6.02 | 6.26 | 6.10 | 6.19 | 829 ± 18 |
| (325 g:1 g) | 5.90 | 5.80 | 5.71 | 5.67 | 721 ± 17 |
| (4.25 g:1 g) | 5.87 | 5.39 | 5.32 | 5.19 | 679 ± 25 |

^aNormalized to 100 g of flour.

^bSALP = Sodium aluminum phosphate.

^cMCP = Monocalcium phosphate.

added to lower the pH to a level comparable to that of the control, the loaf volume decreased with each addition of acid. From these data, it was concluded that pH was not the factor affecting loaf volume.

Effect of Reaction Salts on Loaf Volume

The effect of the salts produced as a result of the leavening reaction was studied. First, loaf volume as a function of salt (NaCl) level was determined. The optimum NaCl level was 1.5–2.0% (Fig. 5), as reported by Finney (1984). A substantial decrease in loaf volume occurred above and below that level. Doughs were then prepared with the salts produced from the MCP plus soda and the SALP plus soda reactions. A substantial decrease (200 cm³) in loaf volume resulted with both leavening acids (Table IV).

We proposed two hypotheses to explain why loaf volume decreased when leavening acids were added to dough. First, the total level of salt was too high and reduced the volume, as previously indicated in Figure 5. The second hypothesis was that specific ions present in the leavening acid were detrimental to loaf volume. To determine whether either or both of these hypotheses were correct, a constant level of reaction salts (produced from 1 g of leavening acid and 1 g of soda) from several acids (all acids used had a neutralizing value of 100) was added to doughs, while the level of NaCl was varied from 0 to 1.5%. From Table V it is clear that as the NaCl level decreased, the loaf volumes of the products made from all three acids increased but not to the control level. Thus, with the level of chemical leavening used in these experiments, the optimum level of NaCl was zero.

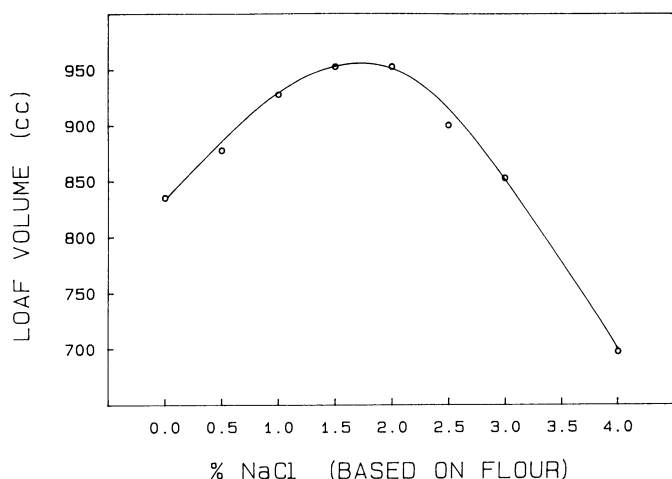


Fig. 5. Effect of NaCl on loaf volume.

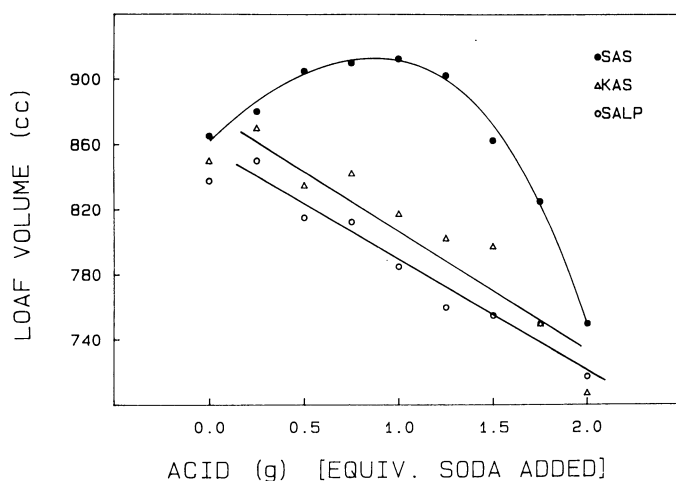


Fig. 6. Effect of levels of reaction salts on loaf volume. Neutralizing value = 100 for all acids.

Next, various levels of different reaction salts were added to doughs that contained no added sodium chloride. Figure 6 shows that the amount and type of salt affected the loaf volume. There was an optimum level (1 g) of sodium aluminum sulfate (SAS) that produced a loaf volume comparable to the control. Above that level the loaf volume was significantly lower. On the other hand, loaves with SALP and potassium aluminum sulfate (KAS) had lower volumes than the control at acid amounts ranging from 0.25 to 2.0 g. In both cases, the highest loaf volumes were obtained with 0.25 g of acid, and as the amount of acid increased the loaf volume decreased. Based on these data, it was speculated that specific ions were detrimental to loaf volume, particularly phosphate and potassium ions.

To better understand the effects of specific ions on gluten structure and loaf volume, mixograph curves were compared to characterize the ions. Kinsella and Hale (1984) reported that anions of the Hofmeister (lyotropic) series alter the classical farinograph patterns of bread flour dough. We used a mixograph to confirm those findings. Table VI shows the various lyotropic ions and their salt levels needed to produce a certain mixograph

TABLE IV
Effect of Reaction Salts on Loaf Volume (Flour A)

| Sample | Loaf Volume ^a (cm ³) |
|--------------------------------------|---|
| Control | 915 ± 5 |
| MCP ^b + soda (1.25 g:1 g) | 705 ± 9 |
| SALP ^c + soda (1 g:1 g) | 713 ± 10 |

^a Based on 100 g of flour.

^b SACP = Sodium aluminum phosphate.

^c MCP = Monocalcium phosphate.

TABLE V
Effect of NaCl Plus Reaction Salts on Loaf Volume (Flour B)

| NaCl Level ^a | SAS Loaf Volume ^{b,c} (cm ³) | SALP Loaf Volume ^{b,d} (cm ³) | KAS Loaf Volume ^{b,e} (cm ³) |
|-------------------------|---|--|---|
| 1.50 | 795.0 ± 5 | 652.5 ± 25 | 777.5 ± 4 |
| 1.25 | 837.5 ± 38 | 637.5 ± 18 | 822.5 ± 38 |
| 1.00 | 817.5 ± 11 | 687.5 ± 4 | 825.0 ± 21 |
| 0.75 | 865.0 ± 2 | 702.5 ± 31 | 825.0 ± 2 |
| 0.50 | 865.0 ± 2 | 707.5 ± 11 | 837.0 ± 4 |
| 0.25 | 892.5 ± 11 | 740.0 ± 2 | 817.5 ± 4 |
| 0.00 | 917.5 ± 25 | 752.5 ± 4 | 817.5 ± 32 |

^a Based on 100 g flour.

^b For each chemical leavening system 1 g of acid was added to 1 g of soda (neutralizing value for all acids was 100).

^c SAS = Sodium aluminum sulfate.

^d SALP = Sodium aluminum phosphate.

^e KAS = Potassium aluminum sulfate.

TABLE VI
Mixograph Study Results on Specific Ions of the Lyotropic Series

| Sample | Salt Level ^a (mg) | Moles × 10 ⁻⁴ |
|--------------------|------------------------------|--------------------------|
| Anionic series | | |
| Sodium citrate | 129 | 4.99 |
| Sodium phosphate | 142 | 9.98 |
| Sodium tartrate | 194 | 9.98 |
| Sodium sulfate | 284 | 20.00 |
| Sodium acetate | 328 | 40.00 |
| Sodium chloride | 339 | 58.00 |
| Sodium bromide | 1,646 | 159.96 |
| Sodium iodine | 3,477 | 232.00 |
| Cationic series | | |
| Calcium chloride | 1,932 | 174.00 |
| Potassium chloride | 432 | 57.94 |
| Sodium chloride | 339 | 58.00 |
| Lithium chloride | 983 | 232.00 |

^a Level needed to produce the specified mixograph curve in Fig. 2.

TABLE VII
Effect of the Amount and Type of Reaction Salt
on Gassing Power and Loaf Volume (Flour B)

| Sample ^a | Gasograph Units | Loaf Volume (cm ³) |
|----------------------|-----------------|--------------------------------|
| Control ^b | 32.0 | 935.0 ± 12 |
| SALP ^c | | |
| 0.25 g | 39.7 | 850.0 ± 2 |
| 0.50 g | 36.5 | 815.0 ± 21 |
| 0.75 g | 35.7 | 812.5 ± 18 |
| 1.00 g | 33.5 | 785.0 ± 14 |
| 1.25 g | 31.2 | 760.0 ± 3 |
| 1.50 g | 31.1 | 755.0 ± 14 |
| 1.75 g | 30.2 | 750.0 ± 14 |
| 2.00 g | 28.8 | 717.5 ± 38 |
| SAS ^d | | |
| 0.25 g | 39.4 | 880.0 ± 14 |
| 0.50 g | 34.7 | 905.0 ± 28 |
| 0.75 g | 35.0 | 910.0 ± 14 |
| 1.00 g | 34.2 | 912.5 ± 11 |
| 1.25 g | 33.0 | 902.5 ± 25 |
| 1.50 g | 32.0 | 862.5 ± 4 |
| 1.75 g | 30.9 | 825.0 ± 21 |
| 2.00 g | 30.8 | 750.0 ± 3 |
| KAS ^e | | |
| 0.25 g | ... | 870.0 ± 7 |
| 0.50 g | 35.5 | 835.0 ± 7 |
| 0.75 g | 35.2 | 842.5 ± 25 |
| 1.00 g | 32.8 | 817.5 ± 17 |
| 1.25 g | 32.8 | 802.5 ± 4 |
| 1.50 g | 33.2 | 797.5 ± 38 |
| 1.75 g | 31.3 | 750.0 ± 5 |
| 2.00 g | 31.0 | 707.5 ± 4 |

^a An equivalent amount of soda and acid was added to each dough.

^b Standard formula.

^c SALP = Sodium aluminum phosphate.

^d SAS = Sodium aluminum sulfate.

^e KAS = Potassium aluminum sulfate.

pattern (Fig. 2). Results with the anionic ions corresponded to the anionic lyotropic series described by Bull (1964). The salt level needed to obtain the specified mixogram progressively increased as the series was followed.

When comparing the salt levels of sodium sulfate to sodium phosphate, half the amount of phosphate was needed to obtain the same mixograph pattern. We can speculate that the effect of these salts on the dough properties, as shown by the mixograph, explains the baking results with SAS and SALP (Fig. 6). In the results of baking with SALP, even at minimal amounts, the salt curve had a negative slope. With sodium sulfate, which is closer in the lyotropic series to sodium chloride, more salt was needed to produce the mixograph pattern. In the baking results using SAS, a 1-g level produced an optimum loaf volume. In SALP doughs, concentrations greater than 0.25 depressed loaf volume. The pattern was not seen with the cationic lyotropic series described by Bull (1964) or of von Hippel and Schleich (1969).

A baking study with selected ions of the anionic lyotropic series was conducted to confirm the mixograph results. Salt levels ranging from 0 to 6% were added to doughs. The baking results also corresponded to the anionic lyotropic series described by Bull (1964) and, therefore, supported the mixograph results (Fig. 7). The figure shows that even at minimal amounts the sodium phosphate salt curve had a negative slope. However, as the series was followed the level of salt for each curve needed to produce an optimum loaf volume increased. For example, the sodium chloride curve had an optimum loaf volume at the 1.5% level, whereas, the NaI curve optimum loaf volume was at 2.5%.

The effect of the amount and type of reaction salt on gassing power was also studied. It is evident from Table VII that, compared to the control, loaf volumes were reduced in doughs when SALP and KAS were added. These data indicate that gas was being produced (i.e., 0.5 g of SALP produced 36.5 GU compared to 32 GU produced by the control) but not retained by the loaves. In the doughs containing SALP and KAS, the lowest acid levels

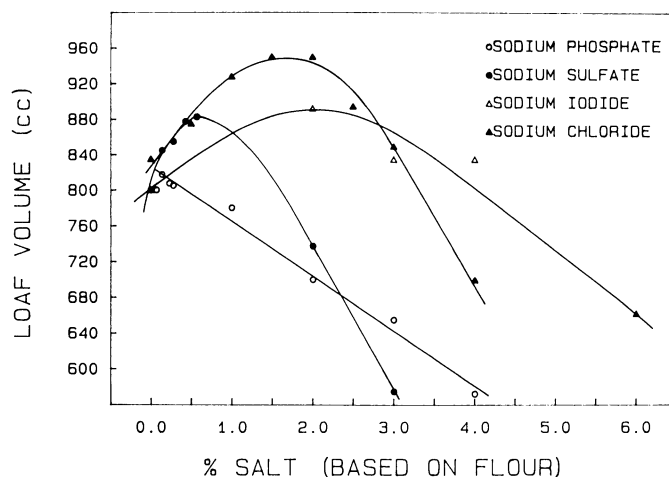


Fig. 7. Baking results of selected ions of the anionic lyotropic series.

produced the highest gassing powers and loaf volumes. However, those loaf volumes were still substantially lower than that of the control. On the other hand, SAS at a 1-g acid level and with a slightly higher gassing power produced a loaf volume comparable to that of the control. This information supports the theory that the addition of the phosphate and potassium ions of SALP and KAS reduces the ability of the dough to retain gas, thereby decreasing loaf volume. However, at appropriate levels, SAS does not impair the ability of the dough to retain gas.

ACKNOWLEDGMENT

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