Modeling the buffer capacity of ingredients in salad dressing products

Madyson Longtin, Robert E. Price, Ritu Mishra, and Fred Breidt

Abstract: The pH of most acid food products depends on undefined and complex buffering of ingredients but is critically important for regulatory purposes and food safety. Our objective was to define the buffer capacity (BC) of ingredients in salad dressing products. Ingredients of salad dressings were titrated individually and in combination using concentrations typical of dressing products. Titration curves from pH 2 to 12 were generated with sodium hydroxide and hydrochloric acid, which were then used to generate BC curves. A matrix of concentration and pK values for a series of monoprotic buffers approximated the pH of each ingredient. Some buffer series required anion or cation corrections for accurate pH prediction, possibly due to the presence of salts of acid or bases. Most buffers had BC values less than 10-fold the BC of acetic acid (0.25 β) typically in dressing formulations and had little influence on the final product pH of the dressings tested. Unexpectedly, we found that sugars in dressing formulations, including sucrose or corn syrup, exhibited buffering at pH values greater than 11 (0.035 β and 0.059 β, respectively), which was likely due to weakly acidic hydroxyl groups on the sugar molecules. However, the concentration and pK for buffers above pH 11 or below pH 2 were difficult to quantify due to the BC of water. The BC data may help to quantify the effects of salad dressing ingredients on the final product pH and benefit regulatory agencies and manufacturers in assessing product pH and safety.

Keywords: acid, base, buffer capacity, ionic strength, modeling, pH prediction, salad dressing

Practical Application: Buffer capacity data for salad dressing ingredients may help determine the influence ingredient addition will have on the final pH of a salad dressing product. The addition of low acid ingredients with little or no buffering may not significantly alter pH. The modeling method may be useful for regulatory purposes to estimate the effects of low acid ingredients on pH changes for food safety and may also be useful for product development of acid and acidified foods.

1. INTRODUCTION

For the formulation of acid or acidified foods, the final equilibrium pH must be maintained at or below pH 4.6. Acid and acidified foods are defined in the U.S. acidified foods regulation, 21 CFR part 114 (FDA, 1979). Acid foods naturally have a pH value below 4.6 and are exempt from regulation under 21 CFR part 114, whereas acidified foods achieve an equilibrated pH below 4.6 by the addition of acid or acid food ingredients to low acid foods (with pH initially above 4.6). Maintaining an equilibrium pH at or below pH 4.6 in these foods is required to prevent botulism (Ito, Chen, Lerke, Seeger, & Unverferth, 1976). Because some acid food products contain only small amounts of low acid ingredients, it may be difficult for a producer to know if a product will be considered acid or acidified. As stated in 21 CFR part 114: "Acid foods (including such foods as standardized and nonstandardized food dressings and condiment sauces) that contain small amounts of low-acid food(s) and have a resultant finished equilibrium pH that does not significantly differ from that of the predominant acid or acid food, and foods that are stored, distributed, and retailed under refrigeration are excluded from the coverage of this part." The acidified food regulations do not define the quantities of a low acid ingredient that can be added to an acid food before it becomes an acidified food. However, this quantity should depend on the pH, the buffer capacity (BC) of the acid foods and the low acid ingredients because the resulting pH change will depend on these factors.

A generalized BC model (Dougherty, Da Conceicao Neta, McFeeters, Lubkin, & Breidt, 2006) has been developed to determine pH and ratios of dissociated and undissociated acids in solutions. This method has been used to determine the amount of selected acid or acids needed for a given protonated acid concentration at a predefined pH (Lu, Breidt, Pérez-Díaz, & Osborne, 2011). In the manufacture of acid and acidified foods, however, estimating pH changes with ingredients having undefined BC remains an important problem. The difficulty of calculating the pH of buffered solutions increases as the number of weak acids or bases in the solution increases, particularly if polyprotic acids are present in mixed acid solutions (Butler & Cogley, 1998). Many acid foods, including dressings, fermented and acidified vegetables, have multiple low acid ingredients added to the final product, each having undefined BC. These foods often have lactic and/or acetic acid present as the primary acidulent, often at 100 mM or greater concentrations (Breidt, Hayes, & McFeeters, 2004; Fleming, Kyung, & Breidt, 1995; Smittle, 2000). Salad dressing products typically

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have acetic or other acids at concentrations of 400 mM or greater in the aqueous phase, and bacterial pathogen reduction for these products has been defined (Breidt et al., 2013). Low acid ingredients in these products have buffering due to the presence of weak acids and bases, including proteins and amino acids, nucleic acids, and other compounds that contribute to buffering and, therefore, may influence the equilibrium pH.

To determine how low acid ingredients may impact the pH of acid food ingredients such as acetic acid solutions in salad dressings, the BC of the ingredients may be measured by titration with a strong acid or base. Our hypothesis was that the buffering capacity of food ingredients (and the impact on pH in solutions) may be estimated using a series of monoprotic buffers that have equivalent buffering to the food ingredient. By comparison of the BC values of low acid ingredients and the BC values of acid ingredients, the impact of the low acid ingredients on the final equilibrium pH of dressing formulations may be estimated. The modeling methods used for this study and the validation of pH prediction for buffer solutions is presented elsewhere (Price et al., 2020). Here we investigate the BC of acid and low acid ingredients typically present in ranch, blue-cheese, and vinaigrette dressing formulations. These data may be useful for estimating the impact on pH of low acid ingredients in salad dressing products. For further details of buffering, p*K*, and the impact of acid and bases on pH of solutions, see Butler and Cogley (1998).

2. MATERIALS AND METHODS

2.1 Salad dressing ingredients

Ingredients from three generic dressing formulations: ranch, blue cheese, and vinaigrette were obtained from commercial sources (Association for Dressings and Sauces, personal communication) for use in this study. Low-acid and acid food ingredients (Tables 1 and 2) were dissolved or suspended individually or in combination at the indicated concentration in de-ionized water corresponding to the water phase (approx. 50%) of dressing products. The initial volume for each titration was between 40 and 60 mL and included the sodium chloride (NaCl) typically added to the dressing product to account for ionic strength effects on p*K*. For ingredients that were used in more than one dressing product, the NaCl concentration for ranch dressing was used. Individual or combined dressing ingredients were mixed with water in the amounts specified in Tables 1 and 2, and the volume of the mixture was recorded as the initial titration volume. For aqueous solutions of individual ingredients that already contained NaCl at concentrations greater than or equal to the dressing formulation NaCl concentration, no additional NaCl was added. For ingredients consisting of particulates such as the spice mixture (black pepper and parsley), a suspension was used for titration. The blue cheese was difficult to prepare for titration due to insolubility and required incubation of the suspension with water (at the concentration in Table 1) for up to 8 hours under refrigeration conditions. Because of similar difficulties, xanthan gum was not titrated. Each solution or suspension was prepared independently for the base and acid titrations. The mean of the initial pH values for the acid or base titrations was reported as initial pH for the ingredient mixture along with the standard deviation.

2.2 Titrations

Titration curves were generated using 40 to 50 mL of a solution or suspension of food ingredients using an automated potentiometric titrator (Model 902; Hanna Instruments, Smithfield, RI, USA) with dual cylinders for sodium hydroxide (NaOH) or hydrochloric acid (HCl) titrants. The NaOH or HCl concentrations used for titrations ranged from 3.12 N to 0.001 N, depending on the buffering present for each ingredient. Separate titration curves were done for the acid and base titrations. Titrator settings included dynamic dosing for pH values between pH 2 and 12, from the initial pH of the solution. The dosing parameters were manually adjusted for each solution to achieve approximately 100 data points for the entire pH range, with a minimum gap (when possible) in the pH values resulting from acid or base addition of <0.1 pH units. Prior to each titration, a purge of the NaOH or HCl cylinders was done to remove any gas bubbles. The titration curve data were output in text format and included a Nx2 matrix with data for volume added (mL, for NaOH or HCl) and the resulting pH. These data were selectively exported to a comma delimited spreadsheet file (.csv file) using a custom Python script (Price et al., 2020) and imported into Matlab as a matrix variable using the built-in Matlab csvread.m function. Other required variables were included as Matlab workspace variables, including the concentrations of the NaOH and HCl used, and the initial titration volume.

2.3 Modeling titration curves and pH prediction

The details of the modeling methods are presented elsewhere (Price et al., 2020). Briefly, the titration data were converted to a BC curve by a sequential derivative process using a custom Matlab function, with BC (β) values from each step in the titration resulting from the change in concentration of the added acid or base divided by the resulting change in pH. To generate a model of the resulting BC curve, a trigonometric regression was used with 15 or more sine-cosine parameter sets. To assure the fit of the predicted curve to the BC data, a custom Matlab function was used to solve a linear algebra matrix of partial derivatives for a squared error function. Finally, a BC model as described by Butler and Cogley (1998; Price et al., 2020) was used to identify a matrix of concentration and p*K* values for a series of hypothetical monoprotic buffers that would result in a BC curve similar to the original data. The matrix was derived using a Matlab constrained nonlinear curve fitting algorithm (fmincon.m) to fit the BC model to the trigonometric model.

2.4 Estimation of pH

Modeling results included the pH predicted by the concentration–p*K* matrix, which was accomplished by a numerical solution of an algebraic equation derived from the combined weak acid equilibrium and charge balance equations for the ions in solution (Butler & Cogley, 1998; Price et al., 2020). By default, all p*K* values equal to or below pH 7 were modeled as acids, and p*K* values above pH 7 were modeled as bases. For some ingredients containing sugars, the pH estimates were done by modeling selected p*K* values above pH 7 as weak acids (as indicated below). The pH predictions from the BC model were done with and without anion (A_n) or cation (C_t) terms for salts of an acid or a base. From the charge balance equation used for the derivation of the pH estimation function (Price et al., 2020), the anion concentrations were included as positive values and cation concentrations were included as negatives, so the concentration values for the combined ion term for salts of an acid or base were recorded in the manuscript as negative or positive values (in millimolar units). The magnitude of this "ion" value, which was estimated separately from the initial pH prediction, may also represent error in the model for the predicted pH from the BC curve.

Table 1–Low acid ingredients.

Low acid Ingredient	Dressing type[a]	Composition[b]	Concentration (%)[c]
Blue cheese	B	Crumbles, Fat 50–54%, Moisture 41–46%, NaCl 2.5 – 4%	21
Corn syrup	G	Dry substance 81% to 82.7%, 60.0 to 67% Dextrose equivalent	15
Liquid sucrose	G	Solids 67% to 68% solution, density is 18.32 g/ml.	15
Salted egg yolks	RB	NaCl 10%	8
Sucrose powder	RBV	Assay 99.9 % Sucrose	7
Garlic puree	G	100% frozen garlic puree	6
NaCl	RBV	Assay 99.7% NaCl	4
Buttermilk powder	RB	Protein 30%, moisture 5%	2
Modified starch	RB	Modified food starch, moisture 10%	1
Garlic powder	RBV	Dehydrated onion powder, hot water insoluble solids 18–20%, moisture <7%	1
Mustard flour	V	Fine powder of the endosperm of *Brassica hirta,* moisture <6%	0.78
Dehydrated minced onion	V	Granulation 2% maximum on US #6 scale, 1% through US #35	0.62
Red bell pepper granules	V	Granulation: 12% on US #8, 6% through US #40, moisture <8%	0.62
Onion powder	RBV	Dehydrated onion powder, hot water insoluble solids 18–20%, moisture <7%	0.6
Propyleneglycol alginate	V	Viscosity (2%) 1,000–1,500 centipoise, drying loss 5–15%, particle size <98% 250 um	0.5
Spices (black pepper and parsley)	RB	Dried piper nigrum L, volatile oil >3%, moisture <13%, Parsley (nd)	0.24
Xanthan gum	RBV	Polysaccharide xanthan gum powder 1%	nd

[a] Dressing type for the indictated component: R, ranch; B, blue cheese; V, Vinaigrette; G, general.
[b] Product description (nd = not determined).
[c] Concentration (percent) used for titration, representative of the dressing water phase.

Table 2–Acid ingredients and salts of acids.

Acid ingredients	Dressing type[a]	Composition[b]	Concentration (%)[c]
Distilled vinegar	RBV	30% acetic acid	12.5
Monosodium glutamate	RB	Assay 99%	1.2
Phosphoric acid	RB	75% phosphoric acid	0.7
Potassium sorbate	RB	Assay 99%	0.24
Citric acid	V	nd	0.23
Sodium benzoate	V	nd	0.14
EDTA	RBV	Assay 99.9%, 1% solution	0.01

[a] Dressing type for the indicated component: R, ranch; B, blue cheese; V, Vinaigrette; G, general.
[b] Product description (nd = not determined).
[c] Concentration (percent) used for titration, representative of the dressing water phase.

2.5 Statistics and data processing

The total sum of squared errors (SSE) was used to report the fit of the BC model to the BC data. Details of the modeling methods and Matlab functions are presented in a companion manuscript (Price et al., 2020). A single Matlab LiveSheet script was used for most of the modeling processes, including generation of the BC curves from titration data, the trigonometric model fit, BC model fit, and pH prediction. The program was run on a Windows 10 Desktop computer with 32 GB RAM memory and a quad core 3.5 GHz processor with Matlab version R2018b. Typically, the algorithm required less than 2 s to run for titrations with up to 200 data points between pH 2 and 12. Output included graphs from of each of the three modeling steps and tables with the derived buffer matrix, as well as model results and parameters with the observed and predicted pH values. The program files are available at: (https://www.ars.usda.gov/southeast-area/raleigh-nc/food-science-research/).

3. RESULTS AND DISCUSSION

Previously, BC has been investigated as an important factor influencing beer fermentations (Li, Liu, Kang, & Zheng, 2015), fermentation disorders in ruminant animals (Hille et al., 2016) water quality (Van Vooren, Van De Steene, Ottoy, & Vanrolleghem, 2001), and the BC of whey in cheese-making (Hill, Irvine, & Bullock, 1985). However, the use of BC to estimate the pH of food ingredient mixtures or determine the influence food ingredients on equilibrium pH of acid or acidified foods has not been previously reported. To address this knowledge gap, we examined the BC of the ingredients in salad dressings, listed in Tables 1 and 2, then applied a modeling approach (Price et al., 2020) to determine how the BC data could be used to predict pH impacts of selected salad dressing ingredients. Ingredients were separated into two categories: acid ingredients and low acid ingredients. The BC curves for the principal acid ingredient (distilled vinegar) and a low acid ingredient (buttermilk powder) are shown in Figure 1. As expected, the distilled vinegar (acetic acid) solution

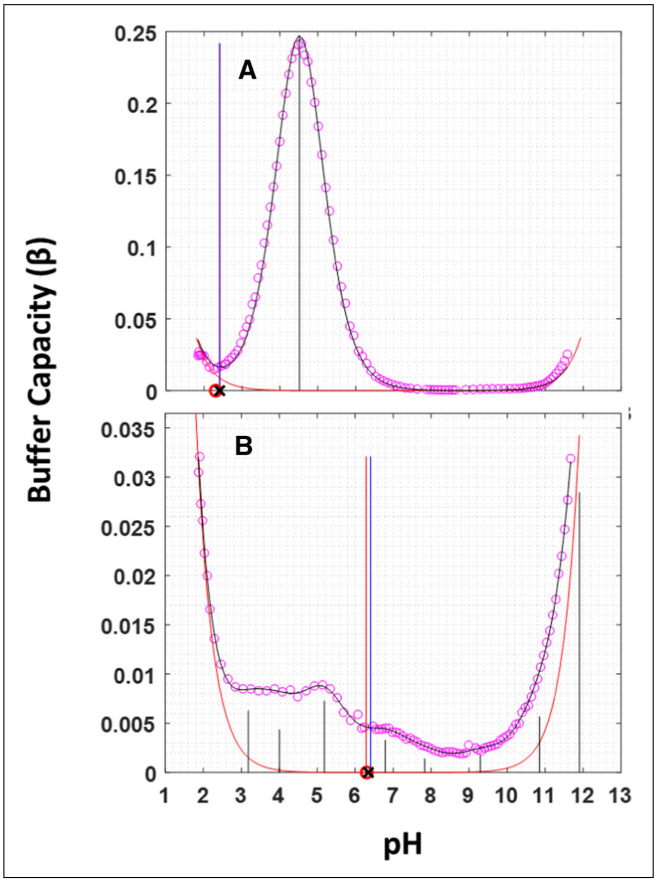

Figure 1–BC of distilled vinegar and buttermilk powder. The BC curve for distilled vinegar (A) and buttermilk powder (B) are shown. The purple circles represent the observed BC data with modifications (insertions and deletions) as described in the methods. The vertical red line represents the starting pH for the acid titration, and the vertical blue line represents the starting pH for the base titration. The fitted black curve represents the BC model fit to the data. The red curve represents the BC of water. The vertical black lines represent the BC value (height) and p*K* (on the *X* axis) of the predicted buffers. The red circle on the *X* axis represents the predicted pH from the model, and the black *X* represents the predicted pH with adjustment for the salt of an acid or base. Please note the difference in the *Y* axis (BC) scales.

had the largest BC value (0.247 β; Table S1) of all the ingredients tested. The estimated concentration for the solution was 429.3 mM. This concentration was roughly equivalent to 2.5% with the range of acetic acid concentrations typical of the aqueous phase of dressing products. This concentration was likely an underestimate, however, as subsequent data have shown that measurement of concentrations above 400 mM acetic acid with this system are subject to a systematic error (Price et al., 2020).

For the acetic acid solution, the unadjusted pH estimation (pH 2.3) was based on the single monoprotic buffer. Optimization of the pH estimate required a 2.35 mM cation adjustment ($C_t = -2.35$) to match the observed pH of 2.41. Note that the estimated pK_a was 4.52, which differed from the published value pK_a for acetic acid of 4.76 at 25 °C in water (CRC, 1995). Using the Davies equation with the coefficients suggested by Butler and Cogley (1998, pp. 49), the adjusted pK_a for 4% NaCl was 4.50. This value was approximately 0.02 pH units less than the observed buffer peak in Figure 1A. The sum of squared error term for fitting the distilled vinegar BC model to the data was among the largest observed (0.06, see Table S2). Although the magnitude of the β values influenced the error term for all ingredients tested, the mean SSE values for each of the three modeling steps (with standard deviation) were $2.9 \times 10^{-5} \pm 1.1 \times 10^{-4}$, $1.16 \times 10^{-2} \pm 0.02$, and $3.5 \times 10^{-3} \pm 0.01$.

The pH for the buttermilk powder solution was 6.35. A total of eight monoprotic buffers were identified for this ingredient, with estimated concentrations ranging from 2.4 to 17.5 mM, and p*K* values between pH 3 and 12 (Table S1). The unadjusted pH value estimated for this buffer series using Eq. 2 with no anion and cation adjustment (i.e., A_n or C_t equal to 0) was pH 6.30, which was 0.05 pH units different from the measured value. A cation addition of 0.2 mM (shown as −0.2 in Table S2) was needed for meeting the observed value. This may be due to a modeling error or indicate that one of the buffers in the 8-buffer series was partially the salt of an acid. The sum of squared error terms for three modeling steps for the buttermilk powder model, including the fit of the trigonometric model data to the BC curve, the BC model to the trigonometric model, and the BC model to the BC curve, were 1×10^{-5}, 5.4×10^{-5}, and 7.9×10^{-5}, respectively (Table S2).

The observed and predicted pH values with and without A_n or C_t adjustment for anion or cation contributions to the pH calculation, as defined (Price et al., 2020) for all of the low acid ingredients are shown in Table 3, and similar data for acid ingredients are shown in Table 4. All ingredients were modeled with 8 or fewer buffers, with only modified food starch having no detectable buffers, that is having the same BC as water. The mean and standard deviation for the number of buffers was 3 ± 2.16 for all ingredients. Excluding the sugar ingredients, the A_n or C_t adjustment varied depending on magnitude of the buffer concentration with a maximum value for cations (C_t) of 55.6 mM for blue cheese and 35.17 mM for anions (A_n) for phosphoric acid. Potassium sorbate and sodium benzoate each had estimated C_t values (14.05 and 11.12 mM, shown as negative values) approximately equal to the estimated buffer concentrations of 14.1 and 11.1 mM (Table 4, respectively). This was expected because these compounds were each prepared as the salt of an acid. For some compounds that had a maximum BC for monoprotic buffers of 5 mM or less, including minced onion, spices, onion powder, propylene glycol alginate, NaCl, and modified food starch, very small (<2 mM) changes in A_n or C_t could result in large changes in pH (up to 3.8 pH units for onion powder). The A_n or C_t ions were not analytically measured for any ingredients, and therefore could represent either chemical constituents of the ingredient (e.g., sodium benzoate and potassium sorbate) or possible inaccuracies in the modeling method. Further work will be needed to distinguish these possibilities.

The buffer composition, including p*K* and corresponding BC value for the monoprotic buffer series for acids and additives in dressing products, is shown in Figure 2. Similar data for low acid food ingredients are shown in Figure 3. Among the acid ingredients, distilled vinegar dominated the buffering, having a β value approximately five times higher than that from the next highest buffer β value as determined from the models for phosphoric, glutamic, or citric acids (0.247 β, vs. 0.049 β, 0.031 β, 0.009 β, respectively). For some ingredients a known BC peak may be split into two, possibly because of modeling algorithm errors. For example, phosphoric acid was found to have four monoprotic buffering components with p*K* values of 1.9, 6.3, 6.7, and 11.35. The two p*K* values of 6.3 and 6.7 likely represent the middle p*K* for phosphoric acid, which has a pK_a of approximately 7.2 in water (CRC, 1995) but an adjusted p*K* (as described above) for 4%

Table 3–Titration parameters and data for low acid ingredients.

Low acid ingredients	Nb[a]	pH_u[b]	pH_i[c]	pK[d]	Conc[e] (mM)	Ion[f] (mM)	SSE[g]
Blue cheese	8	3.43	4.98 (0.38)	3.35	67.93	−3.25	1.68E−03
Sucrose powder	1	12.02	6.20 (0.23)	11.69	41.95	41.95	1.60E−04
Corn syrup	1	11.73	4.61 (0.01)	11.71	25.15	22.00	1.66E−03
Liquid sucrose	3	11.80	4.48 (0.18)	11.50	24.65	18.19	1.47E−03
Buttermilk powder	8	6.30	6.34 (0.08)	11.90	17.50	−2.11	7.87E−05
Garlic puree	5	11.06	5.8 (0.11)	11.43	14.30	15.53	5.65E−04
Mustard flour	4	2.20	6.71 (0.02)	1.93	9.89	−12.01	7.02E−03
Salted egg yolks	5	5.43	6.55 (0.01)	3.67	5.97	−0.01	3.14E−05
Garlic powder	4	5.54	5.50 (0.13)	3.17	5.36	0.03	9.01E−05
Red bell pepper granules	3	2.60	5.17 (0.09)	2.87	5.06	−4.30	3.13E−04
Dehydrated minced onion	5	4.27	5.41 (0.13)	9.17	2.52	0.27	1.92E−06
Spices	4	4.55	5.60 (0.00)	4.13	1.54	−1.07	3.49E−05
Onion powder	2	9.22	5.37 (0.05)	9.04	1.42	0.07	3.55E−05
Propylene glycol alginate	1	4.87	5.32 (0.29)	6.88	0.77	−0.03	6.53E−04
NaCl	4	6.48	5.82 (0.16)	5.19	0.65	0.27	2.30E−04
Modified starch	0	7.00	5.54 (0.28)	nd	nd	0.003	3.77E−04
Xanthan gum	nd	nd	nd	nd	nd	nd	nd

[a] Number of monoprotic buffers identified by the model.
[b] Estimated pH unadjusted for the ion concentration (i.e., salt of an acid or base).
[c] Measured pH of the solution (mean of two measurements).
[d] pK of the monoprotic acid or base with the highest concentration.
[e] mM amount of the monoprotic acid or base with the highest concentration.
[f] Concentration of anion (+) or cation (−) needed to match the measured pH.
[g] Sum of squared error term for the fit of the BC model to the BC data.

Table 4–Titration parameters and data for acids and acid salts.

Acid ingredients	Nb[a]	pH_u[b]	pH_i[c]	pK[d]	Conc[e] (mM)	Ion[f] (mM)	SSE[g]
Distilled vinegar	1	2.31	2.41 (0.00)	4.52	429.29	−2.35	5.96E−02
Mono sodium glutamate	4	3.73	6.64 (0.07)	4.10	48.55	−27.68	1.17E−03
Phosphoric acid	4	2.34	1.61 (0.04)	1.93	37.26	35.17	3.47E−03
Potassium sorbate	1	3.06	7.16 (0.40)	4.51	14.07	−14.05	1.12E−03
Citric acid	3	2.39	2.51 (0.10)	4.51	13.36	−1.71	3.18E−04
Sodium benzoate	1	2.82	6.97 (0.10)	3.90	11.12	−11.12	3.83E−05
EDTA	1	2.99	6.82 (0.38)	4.21	10.26	−10.25	6.75E−04

[a] Number of monoprotic buffers identified by the model.
[b] pH unadjusted for the ion concentration (i.e., salt of an acid or base).
[c] Measured pH of the solution (with standard deviation).
[d] pK of the monoprotic acid or base with the highest concentration.
[e] mM amount of the monoprotic acid or base with the highest concentration.
[f] Concentration of anion (+) or cation (−) needed to match the measured pH.
[g] Sum of squared error term for the fit of the BC model to the BC data.

NaCl of 0.692. Similarly, the monosodium glutamate BC curve included two monoprotic buffer pK peaks 0.6 pH units apart (at pH 9.06 and 9.56), where one peak was expected at 9.47, or adjusted for 4% NaCl, approximately 9.2. As expected, these compounds required anion (phosphoric) or cation (monosodium glutamate) adjustment, so the effect of the split pK peaks on predicted pH was difficult to assess. Figure 3 shows that the majority of low acid ingredients had monoprotic buffer values from the model below 0.01 β. Blue cheese had the highest overall buffering among low acid ingredients, with BC values ranging from 0.063 β to 0.019 β.

The sucrose powder solution exhibited an unexpected buffering peak with a single pK value of 11.7 and an unadjusted predicted pH value of 11.97. Therefore, a 41.9 mM anion (A_n) adjustment was needed to match the observed pH of 6.20 ± 0.23 (Figure 4, Tables S1 and S2). The model results for the other sugars tested also showed similar buffering characteristics, with corn syrup and liquid sucrose having buffer pK values above pH 10 at concentrations up to 50 mM (Tables S1 and S2) and correspondingly large anion adjustments to correct the predicted pH. By default, these buffers were modeled as bases because the pK was above 7. However, when the pH for the sucrose powder was modeled using the pK_a of 11.7 as an acid instead of a base, an estimated pH of 6.39 (for pH 6.2 observed) was obtained. Similarly, liquid sucrose had an observed pH of 4.47 ± 0.18 but a predicted pH of 11.73, respectively, but when the buffer was modeled as a weak acid, the predicted pH was 4.30. The pH estimate was also influenced by a weak acid buffer with a pK of 5.6 of approximately 0.7 mM (Table S1). With corn syrup, however, the observed and predicted pH values with this approach were 4.61 and 6.1, respectively. It is possible there was also a weak buffer estimated around pH 5.6, similar to what was observed for liquid sucrose. Unfortunately, the titration data in this pH region was not accurately measured for corn syrup, due to the proximity of pH 5.6 to the start of the titration curves, pH 6.1. Interestingly, sugars may be considered to be polyprotic weak acids with acidic hydroxyl groups that have pK values above 11 or 12 (Feng, Bagia, & Mpourmpakis, 2013; Urban & Shaffer, 1932). These data indicate that further improvements may be needed for the model, to correct the pH estimates, particularly for sugars and possibly other compounds having weak acid pK values above neutral pH.

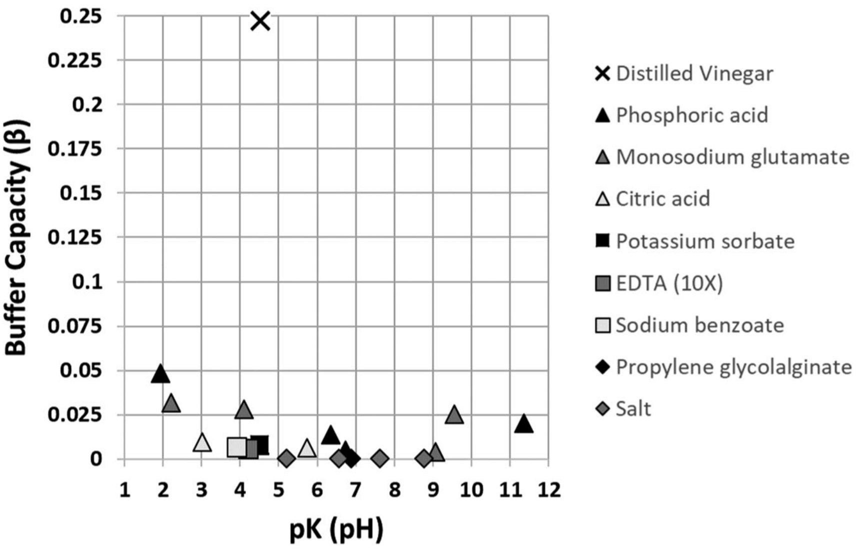

Figure 2–The BC of dressing additives compared to acetic acid. The *x* is the predicted BC value for acetic acid. The symbols represent the BC values for the monoprotic buffers predicted for: phosphoric acid (black triangle); monosodium glutamate (dark gray triangle); citric acid (light gray triangle); potassium sorbate (black square); EDTA (dark gray square); sodium benzoate (light gray square); propylene glycol alginate (black diamond); salt (NaCl, dark gray diamond).

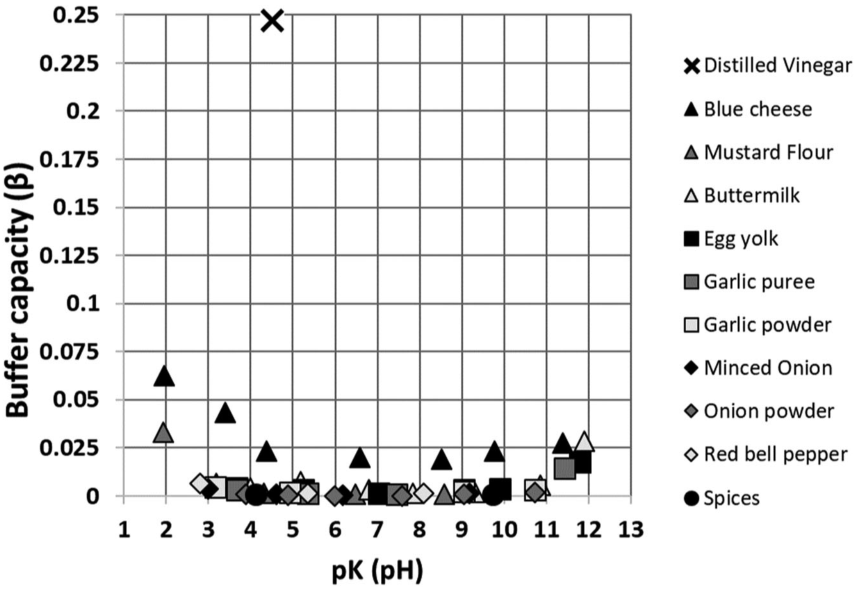

Figure 3–The BC of low acid ingredients compared to acetic acid. The *x* is the predicted BC value for acetic acid. The symbols represent the BC values for the monoprotic buffers predicted for: blue cheese (black triangle); mustard flour (dark gray triangle); buttermilk powder (light gray triangle); egg yolk (black square); garlic puree (dark gray square); garlic powder (light gray square); minced onion (black diamond); onion powder (dark gray diamond); red bell pepper (light gray diamond); spices (black pepper and parsley, black circle).

Because of the increase in the buffering of water at pH values below pH 2 and above pH 12, we were not able to determine a clear peak for buffers that had p*K* values near the ends of the titration curves. For this reason, the p*K* and concentration values for buffers near the ends of our titration curves should be considered only as estimates and may be subject to variation due to small differences in the end points for the titration curves and upper and lower pH limits for the modeling algorithm. However, because the presence of buffering above pH 11 for sugars was likely due to the weakly acidic sugar hydroxyl protons, these acidic groups should not significantly affect pH of salad dressings.

The ability to make predictions about pH values with ingredient mixtures is potentially a useful feature of the BC modeling approach. We therefore examined mixtures of ingredients with measured BC values. To determine the difference in the buffering capacity between acid ingredients in the ranch dressing product and the other food ingredients, selected mixed ingredient samples were prepared and titrated. The acid ingredient mixture for the ranch dressing formulation included: distilled vinegar, phosphoric acid, monosodium glutamate, potassium sorbate, and ethylenediaminetetra-acetic acid (EDTA; Table 2, Figure 5A). As with other ingredient mixtures, NaCl and water were added as described above. The second mixture was similarly prepared but contained all the ingredients indicated for ranch dressings (Tables 1 and 2, Figure 5B) with the exception of xanthan gum. The BC curve for the acid ingredients was found to require five monoprotic buffers for the model curve, representing a composite of all buffering ingredients. A similar set of buffer values was found for the BC model of the mixture with all ingredients, with two differences; an additional buffer was needed with a p*K* value of 3.4, and the β value for the highest p*K* buffer increased from 0.04 β for the acid ingredients to 0.06 β, along with a corresponding difference in pK_a from pH 11.6 to 11.4. A reasonable assumption to explain this difference in the BC curves is the presence of the

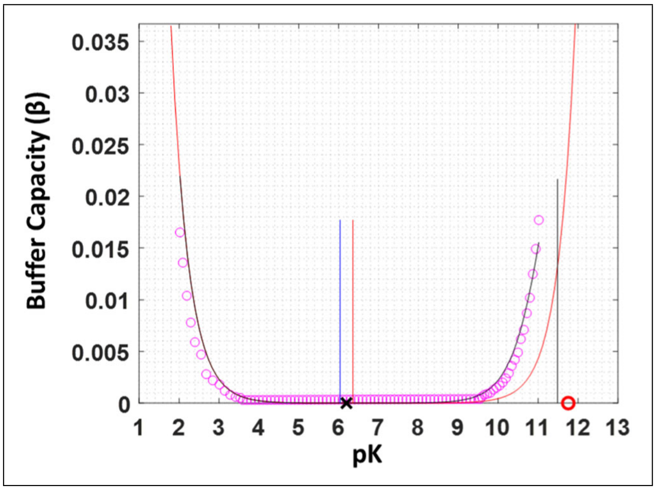

Figure 4–BC of a sucrose solution. The purple circles represent the observed BC data with modifications (insertions and deletions) as described in the methods. The vertical red line represents the starting pH for the acid titration, and the vertical blue line represents the starting pH for the base titration. The fitted black curve represents the BC model fit to the data. The red curve represents the BC of water. The vertical black line represents the BC value (height) and p*K* (on the *X* axis) of the predicted buffer. The red circle on the *X* axis represents the predicted pH from the model, and the black *X* represents the predicted pH with adjustment for the salt of an acid or base.

Table 5–Ingredient combinations.

Ingredient[a]	Calc pH[b]	Measured[c]	ΔpH[d]
(A) Acid ingredients	3.05	3.08 (0.03)	−0.03
(B) Buttermilk powder	6.35	6.34 (0.08)	−0.001
(B10) Buttermilk powder-10×	6.35	nd	nd
(C) Citric acid	2.41	2.51 (0.10)	−0.09
Mixtures			
A+B	3.34	3.29 (0.05)	0.05
A+B10	4.09	4.19 (0.01)	−0.10
B+C	4.00	3.69 (0.14)	0.31

[a] Ingredient or mixture code.
[b] The calculated pH from the BC matrix or combined matrices.
[c] The measured pH with standard deviation.
[d] Difference between calculated and measured pH.

sucrose powder in the ranch dressing formulation, which had a p*K* value of 11.7, as described above (presumably representing the weakly acidic hydroxyl groups). These data show the similarity in buffering between the dressing formulations with and without the low acid ingredients, as there was only a 0.3 pH unit difference in the observed pH values between the acid ingredient formulation, pH 3.08 ± 0.025, and the formulation with all ingredients, pH 3.36 ± 0.16. For each mixture, the predicted (unadjusted, without an A_n or C_t correction) pH values were within 0.06 pH units of the mean observed values (Figure 5, Table S2).

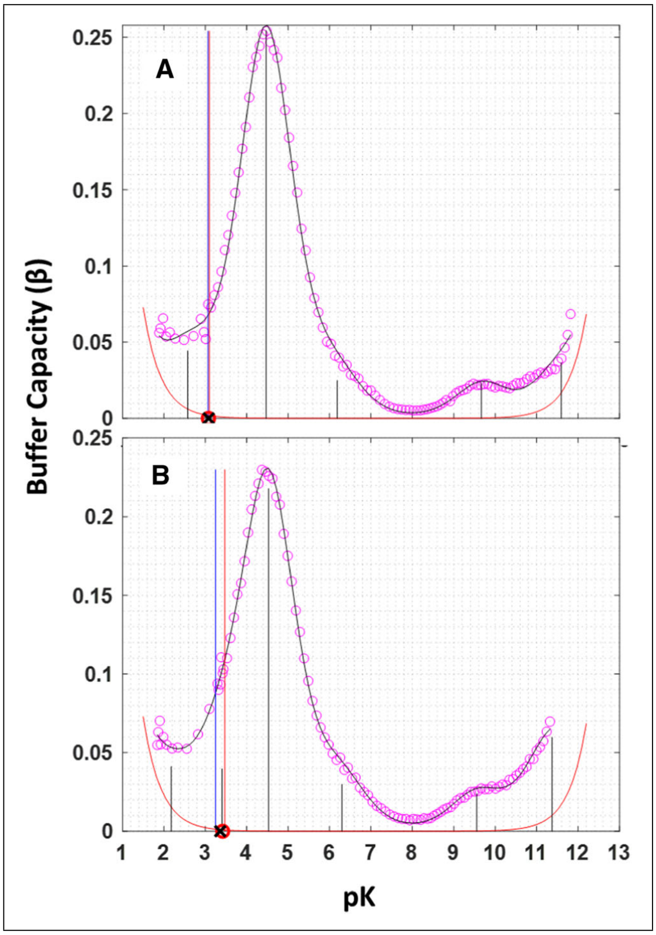

Figure 5–BC of ranch dressing ingredients. Panel A shows the BC model for the combined acid ingredients, panel B shows the BC model for all ingredients. The purple circles represent the observed BC data with modifications (insertions and deletions) as described in the Methods. The vertical red line represents the starting pH for the acid titration, and the vertical blue line represents the starting pH for the base titration. The fitted black curve represents the BC model fit to the data. The red curve represents the BC of water. The vertical black lines represent the BC value (height) and p*K* (on the *X* axis) of the predicted buffers. The red circle on the *X* axis represents the predicted pH from the model, and the black *X* represents the predicted pH with adjustment for the salt of an acid or base.

Because buffer capacity models for acid and base solutions are theoretically additive (Butler & Cogley, 1998), we compared the pH estimates from combined BC models with measured pH values for mixed ingredients. To estimate the pH resulting from selected ingredient mixtures, we used ingredients with predicted pH values differing by more than 3 pH units (Table 5). The acid ingredient mixture (as described above and shown in Figure 5) and buttermilk powder solution had mean measured pH values of 3.08 ± 0.03 and 6.35 ± 0.08 (respectively). For a mixture of buttermilk powder with the acid ingredients, the calculated pH from BC modeling was pH 3.34 (Table 5). The measured pH for mixture of buttermilk powder with the acid ingredients was pH 3.29 ± 0.05, approximately 0.05 pH units lower than the calculated pH. To determine how increasing the concentration of buttermilk powder would affect, the pH prediction when it was combined with the acid ingredients, we multiplied all the concentrations in the BC matrix for buttermilk powder by a factor of 10 prior to calculating the pH. The calculated pH compared with the measured pH for this 10× concentration mixture were pH 4.09 and 4.19, respectively (Table 5). These data indicate that a 10-fold increase in the buttermilk powder concentration (one of the low acid ingredients with the most buffering in the dressing formulation) would not raise the pH above pH 4.6.

The measured pH for a citric acid was 2.50 ± 0.01. For a citric acid and buttermilk powder mixture, the BC modeling data predicted a pH of 4.00, whereas the measured pH for this mixture was pH 3.69 ± 0.14, a difference of approximately 0.31 pH units. Differences between the calculated and measured pH values may have resulted from changes in ion concentrations for salts of an acid or base, although the estimated ion concentrations

(Table S2) were less than 3 mM (all were predicted to be cations) for buttermilk powder, citric acid, and the acid ingredient mixture (Table S2). These data indicate that the BC matrix data may be useful for predicting pH of mixtures of ingredients. Further work will be needed to validate use of the modeling data for ingredient combinations, and assess how ion concentration changes and other factors may influence the pH predictions.

4. CONCLUSIONS

The results show buffering capacity can be used to determine how low acid ingredients may influence the pH of dressing products containing acetic acid as the primary acid and selected low acid ingredients. The results have helped validate the BC modeling method based on a series of monoprotic buffers to predict pH of individual or mixed ingredients. We found that most salad dressing ingredients have little or no buffering capacity compared to acetic acid in the dressing formulations. The majority of monoprotic buffer values for dressing ingredients were 0.01 β or less, compared to 0.25 β for acetic acid. Blue cheese and buttermilk powder, however, had β values of 0.062 and 0.028 for pK values of 1.95 and 11.08, respectively. The data have also helped identify potential improvements for the modeling of food ingredient pH, including the need to address the presence of weak acids with pK_a values above neutral pH, such as sugar hydroxyls. In general buffers with pK values below pH 2 or above pH 11 were difficult to estimate because of the interference from the BC of water at the extremes of pH values. Between pH 2 and 12 in the range for our model predictions, there is essentially no buffering from water that will affect pH.

The low acid ingredients analyzed in this study had pH values near neutral pH and did not contribute strongly to buffering compared to the acid ingredients tested. These results indicate that most of the low ingredients have little influence on the final product pH of the dressing products tested. The data may be useful to industry and regulatory agencies as a means to quantify the amounts of the low acid ingredients that may be added to an acid food while having only a small change in pH (as defined in 21 CFR part 114). Future work will include the use of BC buffer data for estimating the pH changes in acid foods with combinations of low acid food ingredients.

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AUTHOR CONTRIBUTIONS

Author Price managed all laboratory work, and author Longtin was principally responsible for the ingredient preparation and titrations. Author Mishra was instrumental (with ADS) in determining dressing ingredient formulations use for the study. Author Breidt was responsible for the methodology and experimental design. All authors contributed to writing the manuscript and preparation of the figures and tables.

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Supporting Information

Additional supporting information may be found online in the Supporting Information section at the end of the article.

Table S1.

Table S2. Modeling parameters and data for dressing ingredients.