

Buffer Capacity as a Predictive Tool in Food Product Development

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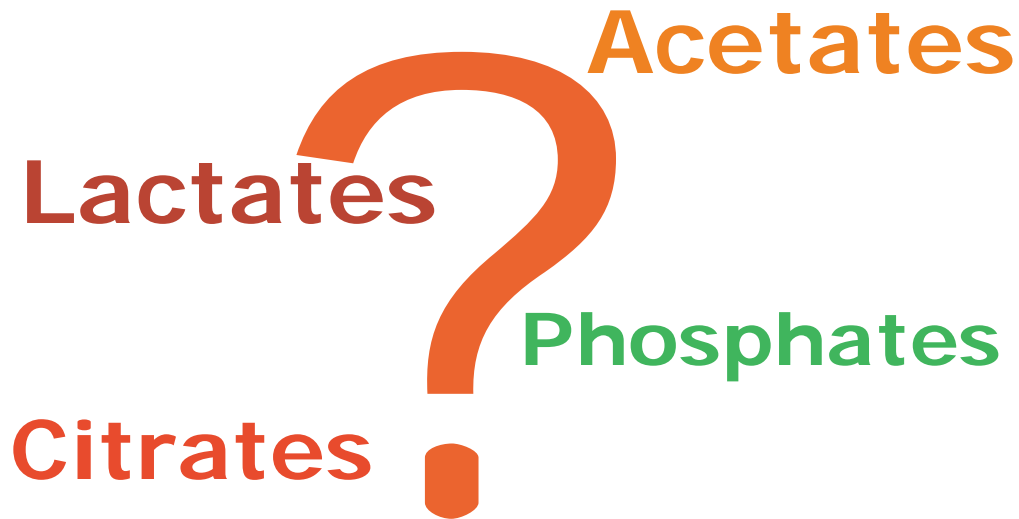
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Good morning and welcome. I am Dan Sortwell, Senior Food Scientist with Bartek Ingredients Inc., Ontario, Canada.

I will be discussing buffer capacity as a predictive tool in food and beverage product development.

Bartek Ingredients Inc. manufactures Malic Acid, Fumaric Acid, and Calcium Fumarate at its plant in Stoney Creek, Ontario, Canada.

How do you know
which buffer salt to choose?



The question of the day is: which buffer salt to use for a given application?

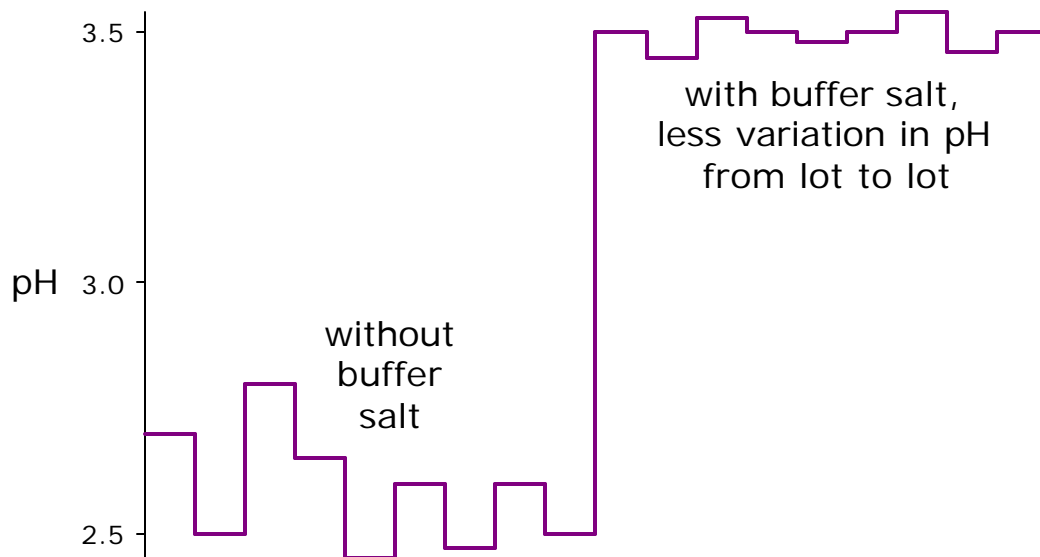
As shown here, there are many different buffer salts to choose from.

Buffer salts and buffer systems are used to:

- improve aspartame stability
- control gelling in pectin-based products
- reduce the rate of sucrose inversion
- reduce the variation in pH and therefore colour and flavour in food and beverage systems
- reduce the variation in pH and therefore texture in gelled products

A buffer system would include acid(s) as well as buffer salt(s). For example, in a hard candy that contains Malic Acid and Sodium Lactate, the buffer system would refer to the combination of Malic Acid and Sodium Lactate used. Both would contribute buffer capacity.

Buffer = partially neutralized acid that resists changes in pH



A buffer is a partially neutralised acid that resists changes in pH.

A buffer can be made by partially neutralising a weak acid like Citric or Malic Acid with Sodium Hydroxide. However, Sodium Hydroxide, or caustic soda, is both hygroscopic and hazardous.

Instead of using Sodium Hydroxide, salts of weak acids such as Trisodium Citrate, Sodium Lactate, Trisodium Phosphate, or Sodium Acetate are used to partially neutralise the acid. Since they also contribute buffer capacity themselves, these salts are buffer salts.

As shown here, the variation in pH from lot to lot is reduced after the addition of a buffer salt. The buffer salt has increased the buffer capacity of the buffer system and this stabilises pH.

Buffer capacity = the amount of acid or base needed to change pH

$$BC = \frac{dC_b}{d(\text{pH})} = \frac{-dC_a}{d(\text{pH})}$$

Normal concentration
(equivalents/liter)
of strong acid or
base that changes
pH by 1.0

Buffer capacity is a measurement of resistance to change in pH and is the amount of strong acid or base required to change pH.

The basic equation is a derivative of added base or added acid with respect to pH. C_b is the normal concentration (equivalents/liter) of added strong base and C_a is the normal concentration (equivalents/liter) of added strong acid. A negative sign is used for C_a because pH decreases when acid is added. Buffer capacity is always positive.

Buffer capacity is expressed as the normal concentration (equivalents per liter) of strong acid or base that changes pH by 1.0.

Target pH determines buffer salt level of use

Buffer salt	Level Required to Achieve pH 3.35 (% w/v)*	Sodium Level (% w/v)
Sodium Lactate	0.14	0.029
Trisodium Citrate dihydrate	0.12	0.028
Trisodium Phosphate	0.07	0.029

*Each buffer salt was added to a mixed solution of Citric Acid (0.16% w/v) and Malic Acid (0.05% w/v)

Going back to the question “which buffer salt to use for a given application?”, one consideration would be the level of use of the buffer salt.

Here, the level of use for three different buffer salts was determined experimentally by adding the buffer salt to a mixed solution of 0.16% w/v Citric Acid and 0.05% w/v Malic Acid until the pH reached 3.35. This was to simulate a situation where the pH of a beverage containing aspartame and a combination of acidulants is raised to 3.35 in order to improve the stability of the aspartame.

As shown here, Trisodium Phosphate had the lowest level of use by far. All three buffer salts contributed the same amount of Sodium. In most cases, it is advisable to minimize the cation level since cations can detract from the flavour profile and interfere with gelling agents.

Trisodium Phosphate would be the logical choice based on use level and assuming no adverse flavour effects. However, before making this decision, it would be useful to know how these buffer salts differ in buffer capacity. To minimise pH variation, the buffer salt with the highest buffer capacity should be chosen.

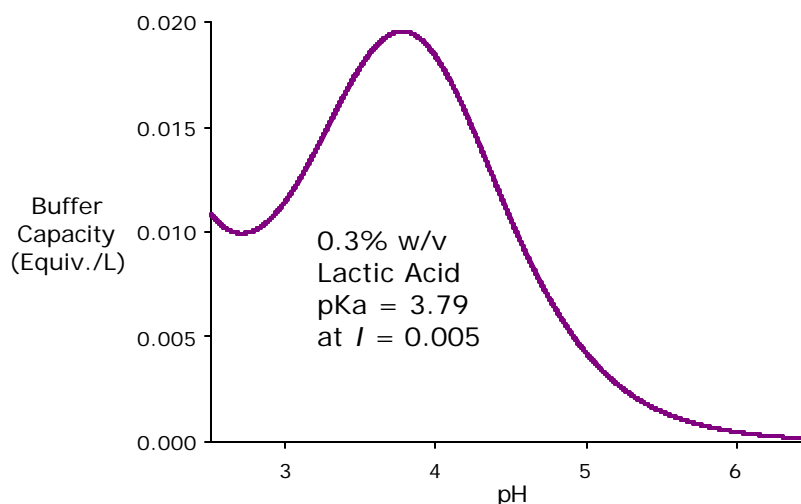
Buffer capacity for a monoprotic acid or buffer salt

$$\text{BC (monoprotic acid)} = 2.303 \left(\frac{K_w}{[\text{H}^+]} + [\text{H}^+] + \frac{C_T K_a [\text{H}^+]}{(K_a + [\text{H}^+])^2} \right)$$

$$[\text{H}^+] = 10^{-\text{pH}}$$

$$K_a = 10^{-\text{pKa}}$$

From Urbansky
& Schock, 2000



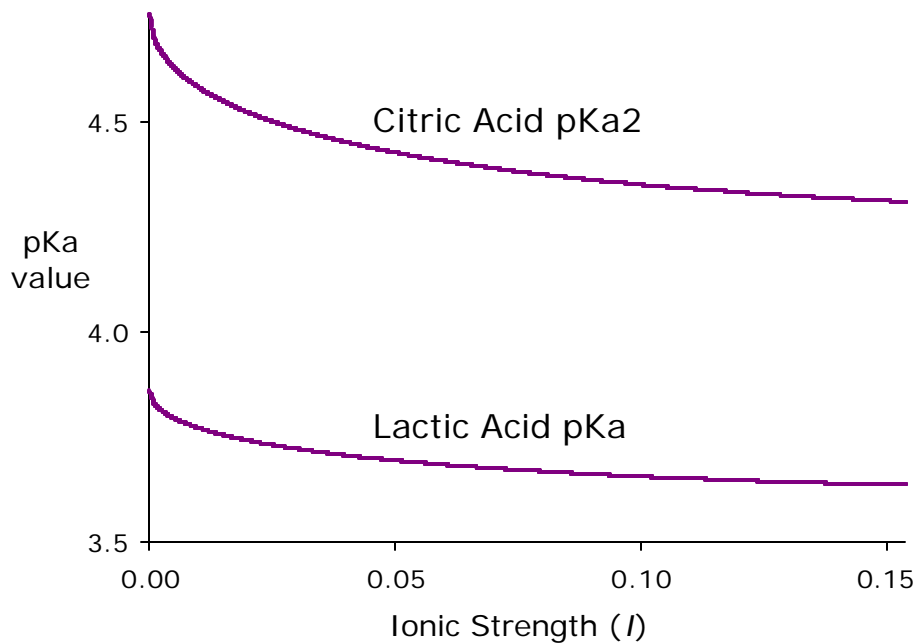
Shown here is an equation for the buffer capacity of a monoprotic acid and/or buffer salt. This equation was derived by Urbansky, E. & Schock, M., 2000 (Understanding, deriving, and computing buffer capacity. *J Chem. Educ.* 77:1640-1644).

In this equation, C_T is the molar concentration of the acid and/or buffer salt. Buffer capacity increases with C_T . Therefore, acids and/or buffer salts with a low molecular weight such as Acetic Acid or Lactic Acid or their respective salts have an advantage in terms of buffer capacity.

The first two terms in the equation represent the molar concentration of hydroxide ions and hydrogen ions. At pHs below 3.0 and above 11.0, these contribute significantly to buffer capacity, as shown for pHs below 3.0 by the curve in the graph for Lactic Acid. This curve was constructed using the equation above.

Note that buffer capacity peaks at the pKa value of the acid, 3.79.

pKa values decline as ionic strength increases



pKa values decrease with ionic strength, as shown by these curves. The curves were constructed using the equations of Butler, J., 1998 (*Ionic equilibrium: solubility and pH calculations*. John Wiley & Sons, New York) and pKa values from Smith, R. & Martell, A., 1989 (*Critical Stability Constants*. Plenum Press, New York)

Deionized water has an ionic strength of zero. The thermodynamic pKa values at an ionic strength of zero are the values shown in most reference books. However, since most food and beverage products contain ionic species and therefore have an ionic strength greater than zero, these pKa values are invalid in most cases.

If the concentration of the ionic species and the pH are known, then it is possible to calculate the ionic strength. The correct pKa values can then be calculated from the ionic strength using Butler's equations. These pKa values are required to calculate buffer capacity.

An isotonic beverage would have an ionic strength of close to 0.154. Calcium fortified beverages containing 10% of the U.S. Calcium RDI could have an ionic strength of 0.05. A typical beverage containing no mineral salts would have an ionic strength of 0.005.

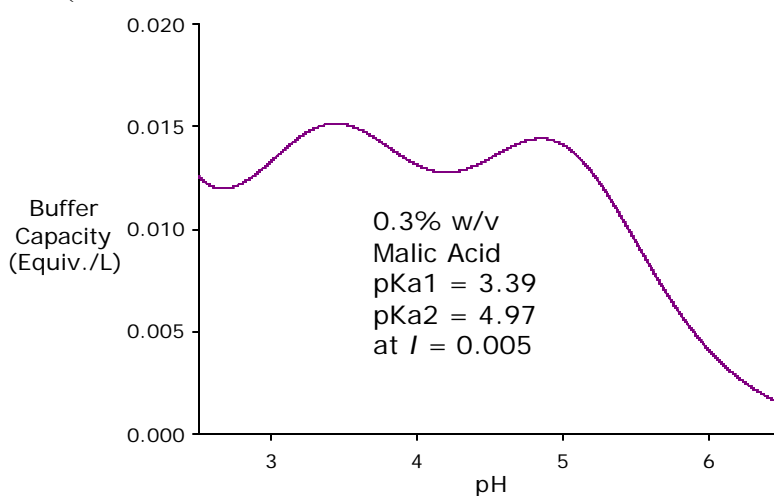
Buffer capacity for a diprotic acid or buffer salt

$$\text{BC (diprotic acid)} = 2.303 \left(\frac{K_w}{[\text{H}^+]} + [\text{H}^+] + \frac{C_T K_{a1} [\text{H}^+] (K_{a1} K_{a2} + 4K_{a2} [\text{H}^+] + [\text{H}^+]^2)}{(K_{a1} K_{a2} + K_{a1} [\text{H}^+] + [\text{H}^+]^2)^2} \right)$$

$$K_{a1} = 10^{-\text{pKa1}}$$

$$K_{a2} = 10^{-\text{pKa2}}$$

From Urbansky
& Schock, 2000



Shown here is an equation for the buffer capacity of a diprotic acid and/or buffer salt. This equation was derived by Urbansky, E. & Schock, M., 2000 (Understanding, deriving, and computing buffer capacity. *J Chem. Educ.* 77:1640-1644).

In this equation, C_T is the molar concentration of the acid and/or buffer salt. Buffer capacity increases with C_T . Therefore, acids and/or buffer salts with a low molecular weight such as Fumaric Acid or Fumarates have an advantage in terms of buffer capacity.

The buffer capacity curve for Malic Acid was constructed using the equation above.

Note that buffer capacity peaks at the two pKa values of the acid, 3.39 and 4.97.

Buffer capacity for a triprotic acid or buffer salt

BC (triprotic acid) =

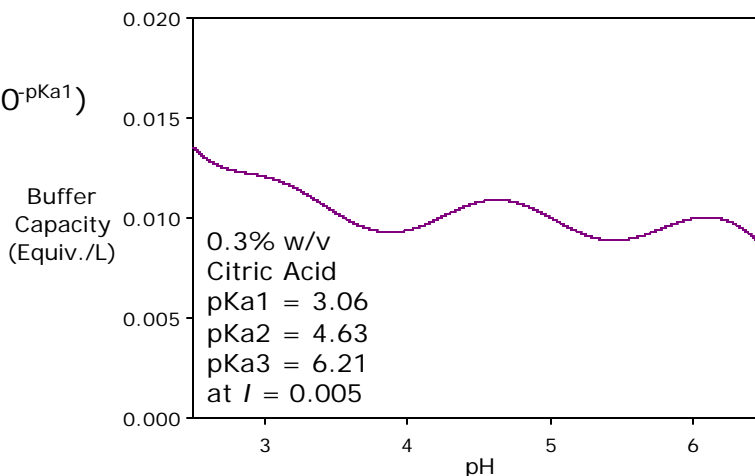
$$2.303 \left(\frac{K_w}{[H^+]} + [H^+] + \frac{C_T [H^+] (\beta_1 + 4\beta_2 [H^+] + (\beta_1\beta_2 + 9\beta_3) [H^+]^2 + 4\beta_1\beta_3 [H^+]^3 + \beta_2\beta_3 [H^+]^4)}{(1 + \beta_1 [H^+] + \beta_2 [H^+]^2 + \beta_3 [H^+]^3)^2} \right)$$

$$\beta_1 = 1/10^{-pK_{a3}}$$

$$\beta_2 = 1/(10^{pK_{a3}})(10^{-pK_{a2}})$$

$$\beta_3 = 1/(10^{pK_{a3}})(10^{-pK_{a2}})(10^{-pK_{a1}})$$

From Urbansky
& Schock, 2000



Shown here is an equation for the buffer capacity of a triprotic acid and/or buffer salt. This equation was derived by Urbansky, E. & Schock, M., 2000 (Understanding, deriving, and computing buffer capacity. *J Chem. Educ.* 77:1640-1644).

In this equation, C_T is the molar concentration of the acid and/or buffer salt. Buffer capacity increases with C_T . Therefore, acids and/or buffer salts with a low molecular weight such as Phosphoric Acid or Phosphates have an advantage in terms of buffer capacity.

The buffer capacity curve for Citric Acid was constructed using the equation above.

Note that buffer capacity peaks at the three pKa values of the acid, 3.06, 4.63, and 6.21.

Experiment used to test buffer capacity equations

Prepare buffer solutions
(pH 4.0; I 0.01, 0.02)



Measure ml. of 1N HCl
required to reduce pH by 1.0



Compare exp. buffer capacity
with calculated values

In order to confirm that these equations could be used to predict buffer capacity, various buffer solutions similar to those used in food and beverage products were prepared. These included single and mixed buffer systems. The pH of these buffer solutions was close to 4.0 and the ionic strength was 0.01 or 0.02.

Buffer capacity was determined experimentally by measuring the ml. of 1 N HCl required to reduce the pH of the buffer solution by 1.0. pH was determined using a Denver Instrument UP-5 portable pH meter with an accuracy of ± 0.01 pH units.

The experimentally determined buffer capacity values were then compared to the values calculated using the equations from Urbansky & Schock.

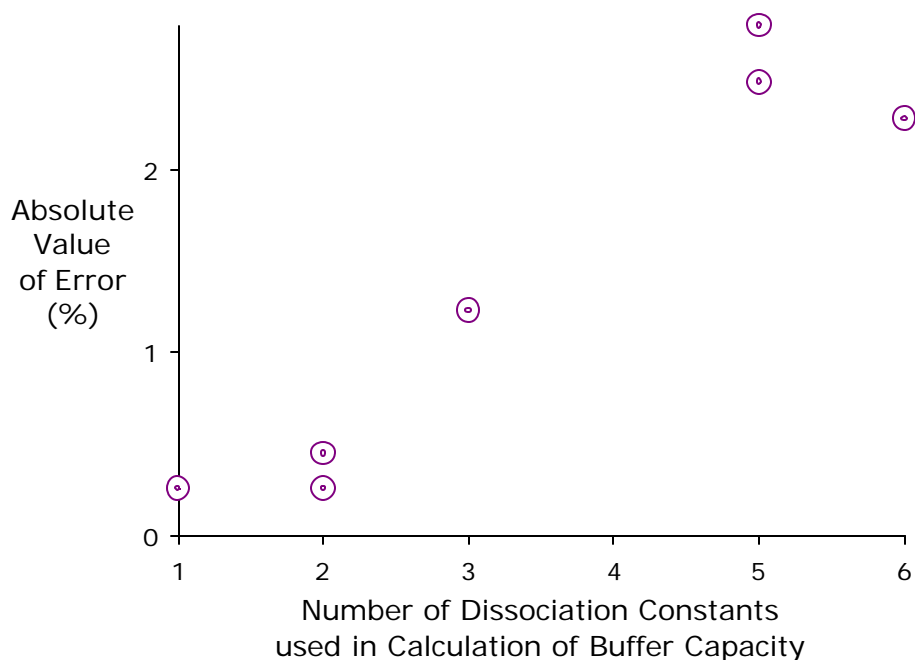
Experimental results were $\pm 3\%$ of calculated values

Buffer composition	Initial pH	Buffer Capacity (Equiv/L)	Error (%)
Lactic Acid 0.037% w/v Sodium Lactate 0.112% w/v	3.97	0.008	0.26
Malic Acid 0.298% w/v NaOH 0.02N	4.01	0.013	0.45
Fumaric Acid 0.182% w/v NaOH 0.02N	3.92	0.011	-0.26
Citric Acid 0.222% w/v Trisodium Citrate dihydrate 0.196% w/v	3.88	0.011	1.23
Malic Acid 0.156% w/v Trisodium Citrate dihydrate 0.196% w/v	4.04	0.011	2.48
Malic Acid 0.183% w/v Trisodium Phosphate 0.110 % w/v	3.97	0.009	-2.79
Citric Acid 0.199% w/v Trisodium Phosphate 0.110 % w/v	4.07	0.007	-2.28

Shown here are the initial pH, the experimentally determined buffer capacity, and the % error for each buffer solution calculation. For example, in the last buffer solution, the calculated value was 2.28% less than the experimentally determined value.

Based on these results, the Urbansky & Schock equations can be used to predict buffer capacity $\pm 3\%$. This is adequate for the purpose of comparing food and beverage buffer systems.

The error increased with the number of dissociation constants



As Urbansky & Schock (2000) pointed out, "equilibrium constants generally have at least 1-5% uncertainty". Therefore, the more dissociation constants involved in the calculation of buffer capacity, the higher would be the expected error.

As shown here, the absolute value of the error increased with the number of dissociation constants involved in the calculation.

This was particularly true in the mixed buffer solutions, where 5-6 different dissociation constants were involved.

Compare buffer salts in terms of buffer capacity

Buffer salt	Level Required to Achieve pH 3.35 (% w/v)*	Sodium Level (% w/v)	Est. Total Buffer Capacity (Equiv/L)
Sodium Lactate	0.14	0.029	0.0143
Trisodium Citrate dihydrate	0.12	0.028	0.0113
Trisodium Phosphate	0.07	0.029	0.0095

*Each buffer salt was added to a mixed solution of Citric Acid (0.16% w/v) and Malic Acid (0.05% w/v)

Going back to the problem of choosing a buffer salt for a beverage system at pH 3.35 (described on page five), we are now able to compare the buffer salts in terms of buffer capacity $\pm 3\%$.

The estimated total buffer capacity values shown here were calculated using the equations and include the buffer capacity of the Citric Acid, Malic Acid, and the buffer salt; in other words, the total buffer capacity of each buffer solution at pH 3.35.

As shown here, the buffer capacity of the solution containing Trisodium Phosphate was 33% less than the buffer capacity of the solution containing Sodium Lactate. Trisodium Phosphate was the buffer salt with the lowest use level but also the lowest buffer capacity and therefore the greatest variation in pH.

To determine whether the low buffer capacity of Trisodium Phosphate causes too much pH variation, the pH range of beverage samples with the expected range in titratable acidity would be measured.

Most soluble Calcium salts are buffer salts

Buffer salt	Level Required to Achieve pH 3.35 (% w/v)*	Sodium Level (% w/v)	Est. Total Buffer Capacity (Equiv/L)
Calcium Fumarate trihydrate	0.22	----	0.0167
Sodium Lactate	0.14	0.029	0.0143
Trisodium Citrate dihydrate	0.12	0.028	0.0113
Trisodium Phosphate	0.07	0.029	0.0095

*Each buffer salt was added to a mixed solution of Citric Acid (0.16% w/v) and Malic Acid (0.05% w/v)

Soluble Calcium salts of weak acids such as Calcium Fumarate, Calcium Lactate, and Calcium Gulconate are buffer salts. Neutral Calcium salts such as Calcium Chloride are not buffer salts.

As shown here, if Calcium Fumarate trihydrate, a soluble Calcium salt, is used at 0.22% w/v to provide 10% of the U.S. Calcium RDI in combination with these acids, a pH of 3.35 results and the buffer capacity is even higher than is the case with the other buffer salts.

This is another example of the use of these equations to predict the effect of changes in formulation on buffer capacity.