# Acidity of Milk and Salt Equilibria

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# **Need for determination of acidity of milk**

- The acidity of a solution results from the **ionization of groups that split off or bind protons.**
- Milk being a biological fluid secreted from mammary cells (gland) has to **maintain isotonicity with the blood plasma**.
- Further the proteins in milk exist in its native colloidal state only when the pH of milk is maintained constantly within the given range. Any change in the pH would destabilize the proteins and result in precipitation and gelation.
- The determination of acidity of milk is a **rapid measure to understand the stability of milk during heat processing.**

# **Acidity of milk**

- Freshly drawn milk is **amphoteric to litmus paper**. Which means it will turn the red litmus to blue and blue litmus to red.
- The pH of normal healthy cow milk will range between 6.4 to 6.6 while the pH of buffalo milk is in the range of 6.7 6.8.
- If the animal is suffering from udder disease like **mastitis** the **pH would be higher than the normal milk.**
- In general the pH is lower in colostrum (pH 6.0) and higher in cases of mastitis (Up to pH 7.5) than normal milk of mid lactation.
- Colostrum and mastitis milk differs radically from normal milk because the proportion of proteins and certain salts were observed to be different.
- Milks of low phosphorus, casein, and Ca2+ tend to be low in titratable acidity while excessive acidity is related to hyperketonemia, inadequate calcium and excessive concentrates in the ration

# Types of Acidity

• There are two types of acidity observed in milk

a. Natural acidity or apparent acidity

b. Developed acidity or true acidity

# <u>a. Natural acidity</u>

- Freshly drawn milk from the udder of a cow shows a acidity which is due to its normal constituents. Such acidity is known as Natural acidity or apparent acidity.
- The constituents that contribute to this acidity are Casein, acid phosphates and citrates and to some extent the albumins and globulins, carbon dioxide.
- Colostrum is having high natural acidity due to its protein content.

# a. Natural acidity

- In early lactation acidity is higher which slowly returns to normal level during the second month of lactation. This level is maintained upto the last month of lactation. At that stage of lactation a slight decline in the acidity is observed. This is the normal phenomenon during the lactation of an animal.
- The variation in the natural acidity of fresh milk is due to the species, breed, individual animal, physiological condition of the udder etc. An increase in the solids non fat content of milk would also increase the natural acidity.

## **b.** Developed acidity

During the **microbial multiplication in milk the lactose would be converted into lactic acid** which would result **in increase in the acidity of milk** and decrease in the pH value. This acidity is **known as developed acidity**.

## **b. Developed acidity**

- The sum of natural acidity and developed acidity is known as titratable acidity. The normal acidity of individual cow Milk ranges from 0.10 to 0.26% lactic acid. Milk having titratable acidity more than 0.18% Lactic acid is not suitable to prepare heat treated products as the milk will coagulate at or above that acidity.
- Heated milk will show an increase in acidity due to the changes in the casein complex and formation of acids by the degradation of lactose.
- Dilution of milk will decrease the acidity and increases the pH. The acidity of milk cannot be increased through feeding.

- As a routine method the total titratable acidity is determined by using the **titration method** where the milk sample is **titrated against standard alkali to the phenolphthalein end point.**
- The **pH of phenolphthalein is 8.3 or 8.4**. and at this end point is pink. The color of the **phenolphthalein is colourless in the acidic medium and turned to pink in the alkaline medium.**
- The milk is being titrated using the standard sodium hydroxide and the acidity is determined by calculating the acidity using the volume of the standard sodium hydroxide used for the titrating to the phenolphthalein end point.
- The total titratable acidity of milk is expressed as percent lactic acid.

Titratable acidity of milk could be used in several stages during milk processing, however we have to use it with considerable discretion.

- It is mostly used as a method to grade raw milk at the plant while the milk is received at the milk reception dock (RMRD).
- Titratable acidity could also be of use in monitoring the udder health of an animal. A change in the titratable acidity indicates the change in the udder health.
- It could also be used to study the heat stability of milk during processing.
  Acidity of more than 0.18% lactic acid would result in the curdling during heat processing

#### **Definition of Salt**

Salts are defined as ionic compounds that result from the neutralization reaction of an acid and a base. They are composed of positively charged cations and negatively charged anions in such a proportion that the product formed is electrically neutral i.e. without a net charge.

#### There are several varieties of salts.

i) *Basic salts* : Salts that hydrolyse to produce hydroxide ions when dissolved in water

*ii)* **Acid salts**: Salts that hydrolyse to produce hydronium ions in water

*iii)* **Neutral salts**: Those salts that are neither acid nor basic salts

**Dissolving salts in water would result in the interaction of its ions viz. cations and anions with water. This is called hydrolysis.** This interaction would affect the pH of the solution.

- The cations of strong bases (e.g., Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, etc.) and anions of strong acids (e.g., Cl<sup>-</sup>, SO<sub>4</sub>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> etc.) simply get hydrated but do not hydrolyse. Therefore the solutions of salts formed from strong acids and bases are neutral i.e., their pH is 7. Example: Na<sub>2</sub>SO<sub>4</sub>, KCl, KNO<sub>3</sub> etc.
- Salts formed by reactions of strong acid and weak -base will give acidic aqueous solutions and for e.g.,NH<sub>4</sub>Cl, CuSO<sub>4</sub>, Al(NO<sub>3</sub>)<sub>3</sub> etc. This is due to the interaction of the ions produced from the salt with the ions formed from water. Hydrolysis is quite opposite of neutralization process.

#### **Definition of neutralisation**:

Reaction between acid and base would result in salt formation. This reaction is known as neutralization.

In this reaction water is also formed along with salt. This reaction could be represented as follows

HA	+	BOH-	→ BA	+	H <sub>2</sub> O	
Acid		Base	Salt		Water	

**Depending on the solubility of the salt**, it may **remain in ionized form in the solution or it may precipitate out of solution.** Neutralization reactions usually proceed to completion

#### **Types of Combinations for the Salt Formation**

a. Strong acid and strong base

b. Strong acid and weak base

c. Strong base and weak acid

d. Weak base and weak acid

## a. Strong acid with a strong base

Interaction between a strong acid and a strong base would result in the formation of salt. When strong acid like hydrochloric acid (HCl) reacts with an equally strong base like sodium hydroxide( NaOH) sodium chloride (NaCl) would be formed.

 $HCI + NaOH \rightarrow NaCI + H_2O$ 

The acid and base neutralize each other with the resulting solution will be neutral (pH=7) and there is no interaction between the ions and water.

#### Strong acid with a weak base

The interaction between a strong acid and a weak base would also result in the formation of salt. The following equation expresses this reaction. :

 $HCI + NH_4OH \longrightarrow NH^{4+} CI^- + H_2O$ 

In the solution NH4+ reacts with water

 $NH^{4+} + H_2O \longrightarrow NH_3 + H_3O^+$ 

Ammonia ions formed in this reaction would result in the lowering of pH since they react with water. As such the resulting salt which is in the form of a solution is acidic.

The reaction between a strong acid and a weak base also produces a salt, but water is not usually formed because weak bases tend not to be hydroxides. In this case, the water solvent will react with the cation of the salt to reform the weak base. The equation below represents this reaction. :

HCl (aq) + NH<sub>3</sub> (aq)  $\rightarrow$  NH<sub>4+</sub> (aq) + Cl<sup>-</sup>

 $NH^{4+}(aq) + H \longrightarrow NH_3(aq) + H_3O^+$ 

#### Weak acid with a strong base

Interaction between a weak acid like bleaching powder with a strong base like sodium hydroxide would result in the formation of sodium hypochloride which is a salt. The basicity of this salt is due to the hydrolysis of the conjugate base of the (weak) acid used in this reaction. Similarly sodium acetate formed by the interaction between acetic acid which is a weak acid and sodium hydroxide (NaOH) a strong base will be formed which is a basic salt. When salt is dissolved, ionization takes place: The bleaching powder being a weak acid when it reacts with sodium hydroxide

HClO + NaOH  $\rightarrow$  NaClO + H<sub>2</sub>O

- When a weak acid reacts with a strong base the resulting solution will be basic. The salt will be hydrolyzed to form the acid, together with the formation of the hydroxide ion from the hydrolyzed water molecules.
- NaClO +  $H_2O \longrightarrow HClO + Na^+ + OH^-$

#### Weak acid with weak base

The reaction between the bleaching powder with a weak base like ammonia would form ammonium hypochloride

$$HCIO + NH_3 \leftrightarrow NH_4CIO$$

The pH of the solution formed from the reaction of a weak acid with a weak base depends on the relative strengths of the reactants.

For example, if the acid HClO has a Ka of  $3.4 \times 10^{-8}$  and the base NH<sub>3</sub> has a Kb = 1.6 x 10<sup>-5</sup>, then the aqueous solution of HClO and NH<sub>3</sub> will be basic because the Ka of HClO is less than the Ka of NH<sub>3</sub>. When a salt is formed between a weak acid and a weak base it could be neutral, acidic, or basic depending on the relative strengths of the acid and base.

- If Ka(cation) > Kb(anion), the solution of the salt is acidic
- If Ka(cation) = Kb(anion), the solution of the salt is neutral.
- If Ka(cation) < Kb(anion), the solution of the salt is base