CC7:Unit 8: Technology of Milk

DrB.V.Balasubramanyam
Principal Scientist,DairyTechnology Section,
ICAR- National Dairy Research Institute
Adugodi,Bengaluru-560030

Milk is secreted by all the species of mammals to feed nutrition to their young ones. It also provides immunological properties to the feeding babies. Milk is a dilute emulsion of milk fat combined with colloidal dispersion of proteins with a continuous phase of solution containing lactose minerals and other water soluble solids. In the milk processing industry, the measurement of the physical properties of the milk and milk products are important for designing of the processing equipments (i.e., heat conductivity, viscosity), to determine the concentration of components (i.e., specific gravity, freezing point to determine added water), or to assess the extent of a chemical or physical change (i.e., titratable acidity to know the microbiological changes or viscosity to assess the aggregation of protein miscelles or fat globules). Some of the properties such as colour and taste also plays important role in accepting and grading of milk before it is processed.

Let's learn about the physical properties of Milk under the following sections:

Colour and Taste
pH and buffering capacity
Refractive index
Viscosity
Surface tension
Freezing and boiling point
Specific heat
Electrical conductivity
Oxidation-Reduction (Redox) system and
Lactose - its significance in dairy industry

<u>Colour and Taste</u>

The white colour of milk is due to the scattering of visible light rays by casein miscelles and fat globules. The yellow colour of cow's milk is due to presence of yellow colored pigments i.e, carotenes while the buffalo milk looks whiter due to absence of this component. Homogenization of milk results in a whiter product due to increased scattering of light by smaller, homogenized fat globules. The serum phase of milk is greenish due to the presence of riboflavin which is responsible for the characteristic colour of whey.

Taste

The taste of the milk is generally is a part of flavour. Flavour is defined as the combination of taste and smell. The taster of the milk is both sweet and salty. The sweet taste is contributed mainly from the lactose content while the salt taste is due to the salts present in the milk. The human milk tastes sweeter than cow milk due to presence of higher percentage of lactose in the milk. The fat is the component which contributes to the rich flavour to the milk. Higher the fat, richer the flavour of milk.

pH and Buffering capacity

The pH of milk usually ranges between 6.5 -6.7 with a mean value of 6.6. An important characteristic of milk is its buffering capacity, i.e., resistance to changes in pH on addition of acid or alkali. Milk contains a range of groups which are effective in buffering over a wide pH range. The principal buffering compounds in milk are its salts (particularly soluble calcium phosphate, citrate and bicarbonate) and acidic and basic amino acid side-chains on proteins (particularly of caseins).

The buffering capacity of milk is estimated by determining its titratable acidity, which involves titrating a sample of milk containing a suitable indicator (Phenolphthalein) with NaOH and thus is a measure of the buffering capacity of the between its natural pH and the phenolphthalein endpoint. Calcium and magnesium influence the titration curves of milk because as the pH is raised they precipitate as colloidal phosphates and as the pH is lowered, the colloidal calcium and magnesium phosphates are solubilized. The casein and phosphates account for the major part of the titratable acidity of fresh milk. The increase in titratable acidity in stored milk is due to activity of the microorganisms which converts lactose to lactic acid.

The acid-base equilibrium in milk is influenced by processing operations. Pasteurization causes some change in pH due to loss of carbon dioxide and precipitation of calcium phosphate. Higher heat treatments such as sterilization result in decrease in pH due to degradation of lactose to various organic acids, especially formic acid.

Refractive index

The refractive index of milk at 20^0C is normally in the range of 1.3440 – 1.3485. The refractive index of milk and its total solids content varies with changes in the concentration and composition of the solutes in the milk. Milk contains many dissolved components and fat in emulsion form and proteins in colloidal form, the milk absorbs light of wide range of wavelengths and also scatters UV and visible lights due to presence of proteins. Milk absorbs light of wavelengths between 200 and 380 nm due to presence of proteins and between 400 and 520 due to presence of fat globules particles. Scattering of light by the globular fat particles present in milk has been used to estimate its fat content. The commercial milko-scanners have been developed by using this principle.

Viscosity

The unit commonly used for measuring viscosity of milk is the centipoises (10^{-2} poise)

The viscosity of milk and diary products depends upon the temperature and on the amount and state of the dispersion of solid components. Representative values at 20^0C are: whey 1.2 centipoise (cp) skim milk 1.5 cp and whole milk 2.0 cp. From these values it is evident that the caseinatemiscelles and the fat globules are the most important contribute to the viscosity.

Important factors that influence the viscosity of milk are:

1. State and concentration of protein
2. State and concentration of fat
3. Temperature of milk
4. Age of the milk

State and concentration of the protein

The viscosity of colloidal systems depends upon the volume occupied by the colloidal particles. Changes in the caseinate micelles produced by either raising or lowering the pH results in increased viscosity. The viscosity is approximately doubled by the addition of 10 ml of 1.4 to 3.8 N ammonia to 90 ml milk. Addition of alkali (pH up to11.7), urea (up to 4.8 M) and calcium complexing agents to concentrated (22.7% solids) skim milk causes a marked transient increase of several folds in viscosity followed by a sharp decline. This is due to the swelling of the micelles followed by their disintegration.

State and concentration of fat

Viscosity increases with increasing concentration of fat and solids-not -fat, but consistent general relationship could not be established. Homogenization increases the viscosity of the milk due to increase in number of fat globules in the milk

Temperature

The viscosity of milk and dairy products depends up on the temperature and on the amount and state of dispersion of the solid components. Cooling increases viscosity due to the increased volume of casein micelle and temperatures above 65^0C increase viscosity due to the denaturation of whey proteins. Cooled raw milk and cream exhibit non-Newtonian behavior in which the viscosity is dependent on the shear rate. Agitation may cause partial coalescence of the fat globules (partial churning) which increases viscosity. Fat globules that have under gone cold agglutination may be dispersed due to agitation, causing a decrease in viscosity.

Surface Tension

The surface tension of milk varies between 40 and 60 Newton/meter with an average of about 52Newton/metre. The surface tension of whole milk and skim milk decreases with increase in temperature. It also varies with the age of the milk. The surface tension of rennet whey, skim milk and cream are reported to be 51 – 52, 52- 52.5 and 42 – 54 respectively. The principal surfactant sin milk are proteins, phospholipids, mono and diglycerides. The soluble solids such as salts and lactose does not contribute significantly to the surface tension. Hence the skim milk and whey have higher surface tension and cream has lower values. The surface tension decreases with increase in fat content in milk.

Boiling Point

Boiling point of a solution is the temperature at which the vapour pressure of the liquid equals to the external (Atmospheric) pressure. The water content in fluid milk is highest and hence the boiling point of milk will be close to that of water. But being a collegative property it is influenced by the dissolved substances like lactose, minerals etc and hence it is slightly higher than that of water. Since the vapour pressure of a solution is always less than the vapour pressure of the pure solvent it follows that the boiling point of a solution will always be higher than that of the pure solvent. Pure water boils at 100^0C while the boiling point of normal milk is 100.15^0C.Milk constituents are responsible for the elevation of the boiling point of milk. The normal Ionic↔ molecular ↔ colloidal equilibrium is altered due to heating. Addition of water lowers the concentration of dissolved substances responsible for the reduction in the boiling point. As such adulterated milk with water boils at a lower temperature than the normal milk.

Freezing point

The freezing point of milk, like that of any other aqueous system, depends on the concentration of water soluble components. The average freezing point of bovine milk is usually within the range– 0.512 to – 0.550^0C. The average value for cow milk is close to -0.522^0C, buffalo milk -0.560^0C, sheep milk -588^0C and goat milk -0.575^0C. Freezing point depression of milk is inversely proportional to the souring of milk, fortification of milk with lactose or non fat solids or addition of sugar will increase the depression of thefreezing point. Amount of water added decreases the freezing point depression. Colostrum is having a freezing point -0.605^0C which is slightly less than normal milk due to presence e of more soluble solids. The composition of milk is altered by the udder diseases like mastitis, but in order to maintain the osmotic pressure in equilibrium with blood, the lowering of the lactose content is compensated by increase in the sodium chloride. As such the milk obtained from the animal affected with mastitis will not alter the freezing point.

The freezing point is a property controlled by the number of particles, rather than the kinds of particles, in the solvent. The major components affecting the freezing point are lactose and soluble salts. 75 to 80% of the depression of the freezing point is due to these two constituents. Fat, protein, colloidal calcium phosphate, casein colloids and fat globules have negligible effect on the freezing point of milk because of their high molecular weight.

Specific Heat

The heat capacity of a substance is the quantity of heat required to raise the temperature of a unit mass through a unit range. The term “specific heat” is used almost interchangeably with the “heat capacity”. It is the ratio of heat capacity to that of water at 15^0C (0.99976 cal $g^{-1}C^{-1}$), and thus is dimensionless. The numerical value of specific heat is nearly the same as that of heat capacity. Skim milk exhibits a small but definite linear increase in heat capacity between 1 and 50^0C from about 0.933 to 0.954 cal $g^{-1}C^{-1}$. There is marked decrease in heat capacity as the total solids content of the sample is increased. Dried skim milk products have heat capacity of 0.28 to 0.32 cal $g^{-1}C^{-1}$ in the 18 to 30^0C temperature range. The heat capacity of milk fat in either solid or liquid state is about 0.52 cal $g^{-1}C^{-1}$ and its latent heat of fusion is about 20 cal/g. thus the heat capacity of the cream depends on the fat content in the cream.

Electrical Conductivity

The specific conductance of cow's milk, reflecting its concentration and activity of ions, is on the order of 0.005 $ohm^{-1}cm^{-1}$ at 25^0C. Most normal samples fall in the range of 0.0040 to 0.0055 $ohm^{-1}cm^{-1}$. Higher values usually represent mastitic infections which increase the concentration of sodium and chloride in the milk. Measurement of electrical conductivity has been used for rapid detection of subclinical mastitis disease in milking animals.

The sodium, potassium and chlorides ions of milk are the greatest contributors to its electrical conductivity, sine they are present in the highest concentration. The fat globules in milk reduce the mobility of ion and hence the conductivity of whole milk is less than that in skim milk. The production of acid due to bacterial activity increases the conductivity.

Oxidation-Reduction (Redox) System in Milk

The oxidation reduction reactions involve transfer of electrons between atoms or molecules. Transfer of oxygen (O) or hydrogen (H) or both also may occur. Oxidation is loss of electrons while reduction is the gain of electrons. In a redox system when half of the system is having oxidation reaction and the other half is having a reduction reaction there will be no flow of electrons either in to the system or go out of the system. In normal milk there are several complicated biological systems with varying composition and concentration. In addition to this microorganism gaining entry in to milk contribute certain redox systems to it depending upon the type of the organisms.

Reduction of redox indicators such as resazurin, methylene blue are generally used as an index of the bacterial quality of milk by measuring the reduction time at a suitable temperature of milk containing the dye. The most commonly used method is Methylene Blue Reduction test (MBR time). In this test, a known quantity of methylene blue solution of known concentration is added to 10 ml of milk. Closed air tightly and incubated in water bath maintained at 37^0C. The reduction in blue color is observed at every 30 minute interval till the color of the milk totally turns back to its original white color. The total time taken to complete decolonization is termed as MBR time. Higher the MBR time better the microbial quality of the milk.

Methylene blue is reduced by freshly drawn milk when it is drawn from udder anaerobically indicating a more negative potential than methylene

blue system. Exposure to oxygen will change this potential to be more positive than the mehtylene blue system. Apart from this the chief oxidation and reduction systems present in milk are Ascorbate, lactate and riboflavin.
The concentration of dissolved oxygen is the principal factor affecting the redox potential of milk. Milk is essentially free from oxygen when secreted but in equilibrium with air, its oxygen consent is about 0.3mM

Lactose

Lactose is the carbohydrate which is present in milk of all mammals. It is a disaccharide consisting of glucose and galactose. Its concentration varies widely between the species but almost constant in a particular specie. Lactose content in cow's milk varies between 4.8 to 5.0% while that in human milk varies between 6.5 to 6.7%.
Lactose plays important role in milk and milk products. It is an essential constituent in the production of fermented dairy foods. It affects the texture of the certainconcentrated milk products such as sweetened condensed milk and frozen dairy products and also indigenous diary products such as khoa. It also plays a vital role in heat induced non-enzymatic browning reactions which not only contributes to the colour but also to the flavour the products.

Milk products are especially sensitive to the effects of heat treatment encountered under conventional process and storage conditions because of an abundance of reactive functional groups: aldehyde group of lactose, ε -amino group of lysine and other reactive N-containing groups (e.g. indolyl group of tryptophan, imidazole group of histidine, guanidine group of arginine and theα-amino group of proteins and free amino acids). The most important heat induced changes in dairy products that involve lactose are the changes associated with browning. Milk is the only important naturally occurring protein food with a high content of reducing sugar. Lactose may isomerize or it may react with protein in milk. The reaction of lactose with the caseins and whey proteins of milk systems is the Maillard or non-enzymatic browning reaction. It is also referred to as glycosylation of proteins for e.g. in case of lactose it is known as lactosylation of proteins.
Maillard Type Browning
Generally Maillard types browning is detrimental to the organoleptic, nutritional and functional qualities of the product and are therefore undesirable. However this reaction is being utilized favourably in the preparation of products like khoa where milk is heated in the presence of sucrose to produce brown product with a pleasant flavour. Maillard reaction also plays an important role in the generation of flavour during the manufacture of ghee or clarified butter and milk chocolate.

Factors that influence maillard reactions

The overall rate and product profile of Maillard reaction in foods are highly dependent on number of parameters. However the most important are listed below:

- Reactants
- pH
- Temperature
- Moisture content
- Water activity

Caramelization is a type of non-amino browning reaction. This process consists of heating sugar slowly to around 170°C. As the carbohydrates are heated, the molecules break down and reform into compounds with a characteristic brown colour and flavour. It is a chemical decomposition of non-protein substances that occurs spontaneously at high temperatures and the reaction is known as pyrolysis. Caramelization is a complex, poorly understood process that produces hundreds of chemical products. Caramelization by heat during baking contributes to flavour and colour. However, it occurs to limited extent in milk and milk products and hence has limited significance.

Caramelization is the removal of water from a sugar, by heating. This process results in isomerization and polymerization of the sugars into various high molecular weight compounds. Compounds such as difructose anhydride may be created from the monosaccharides after water loss. The fragmentation reaction of sugars during heating would result in low molecular weight compounds that may be volatile and may contribute to flavour. Polymerization reactions lead to large molecular weight compounds that contribute to the dark brown colour.

Caramelization type of browning may be defined as the heat decomposition of sugars as a function of pH and buffers in the absence of amino compounds. It requires high order of activational energy. Caramelization is the oxidation of sugar by heating resulting in the production of nutty flavour and changing to brown colour. During the process, volatile chemicals are released, producing the characteristic caramel flavour.

Conclusion: Milk is a mixture of soluble, colloidal and emulsion substances distributed in aqueous medium. The physical properties such as thermal conductivity and viscosity are important in designing and operation of the equipments. This property is widely used to detect the subclinical mastitis disease in animals. Elevation of freezing point can be used as an indirect method of detection of adulteration of milk with water. The principle of Refractive index is used in development of milko-scanner for instant detection of fat in milk. Milk contains a range of groups which are effective in buffering over a wide pH range. The principal buffering compounds in milk are its salts and acidic and basic amino acid side-chains on proteins.

Lactose is a disaccharide present only in mammalian milk. It plays an important role in production of fermented milk products. It is also responsible for textural changes in concentrated milks and frozen dairy products. Lactose is the major contributing factor in non-enzymatic browning reaction in the dairy and milk based foods.