

MILK SALTS

- The salts of the milk include those constituents that are present as ions or in equilibrium with ions.
- Main salts of milk are phosphates, citrates, chlorides, sulphates, carbonates and bicarbonates of sodium, potassium, calcium and magnesium. Approx. 20 other elements are found in milk in trace quantities including copper, iron, lead, boron, manganese, zinc, iodine, etc.
- These ions are more or less associated between themselves and with proteins.
- Some metals acts catalysts in oxidation of milk fat leading to oxidative rancidity and certain metals like Ca, P, Mg, Mo, Co, Fe, etc. are components of metalloproteins such as lactoferrin, lactoperoxidase, xanthine oxidase and parts of phospholipids.

- ❑ The salt composition in milk cannot be expressed either as an equivalent to inorganic or organic substance because some salts exist as organic substances also.
- ❑ It is also not possible to express them as ionic substances as a considerable part of these minerals are present in non-ionized form.
- ❑ The ash content of the milk also does not represent the salt composition since during ashing of milk, some of the salts are lost due to volatilization.
- ❑ The minerals in human, cow and buffalo milk play an important role in the availability of these minerals for the young ones. They also play an important role in the digestibility of milk proteins.
- ❑ Na, K and Cl are primarily present as free ions but Ca, Mg, phosphate and citrate are distributed throughout many complexes (highest concentration are CaCit⁻, Mg Cit⁻, H₂PO₄⁻, HPO₄⁻ and CaHPO₄⁻).

IMPORTANT SALTS IN BOVINE MILK

Concentration		
Constituent	Mean (mg/100 g)	Range (mg/100 g)
Cationic		
Sodium	58	47-77
Potassium	140	113-171
Calcium	118	111-120
Magnesium	12	11-13
Anionic		
Total phosphorus	74	61-79
Inorganic phosphorus	63	52-70
Ester phosphorus	11	8-13
Chloride	104	90-127

TRACE ELEMENTS

The large number of trace elements found in milk have significant influence in the various properties of milk and significant role in human nutrition.

Detected in normal bovine milk by spectroscopic and chemical analyses.

The concentration of elements like I, Mo and Zn in the milk exhibit large variation and depends markedly on the diet consumed by the cow. The concentrations of some of them are increased by contamination with utensils and equipment to which milk is exposed while handling and processing.

CONCENTRATION OF TRACE ELEMENTS

Concentration ($\mu\text{g/liter}$)		
Element	Range	Typical Value
Aluminum (Al)	150-1000	500
Arsenic (As)	30-60	-
Barium (Ba)	-	Trace
Boron (B)	100-1000	300
Bromine (Br)	500-20,000	-
Cadmium (Cd)	1-30	-
Cesium (Cs)	-	Trace
Chromium (Cr)	5-80	15
Cobalt (Co)	0.4-1.0	0.5
Copper (Cu)	10-200	75
Fluorine (F)	70-220	-
Iodine (I)	10-1000	-
Iron (Fe)	100-1500	300
Lead (Pb)	20-80	40
Lithium (Li)	-	Trace
Manganese (Mn)	20-100	50
Mercury (Hg)	-	Trace
Molybdenum (Mo)	20-120	70
Nickel (Ni)	0.30	-
Rubidium (Rb)	100-3400	-
Selenium (Se)	4-1200	12
Silicon (Si)	-	~1400
Silver (Ag)	15-50	45
Strontium (Sr)	40-500	170
Tin (Sn)	-	Trace
Titanium (Ti)	-	Trace
Vanadium (V)	-	Trace
Zinc (Zn)	2000-5000	3300

TRACE ELEMENTS	ASSOCIATED/FUNCTIONS
Molybdenum	Found exclusively in xanthine oxidase
Co	Found in vitamin B12
Iron	Essential component of xanthine oxidase, lactoperoxidase and catalase
Copper	Oxidation of milk lipids
Zn (85%)	Associated with casein micelles Alkaline phosphatase, a Zn-containing enzyme, is located primarily in the fat globule membrane but accounts for only a small fraction of the total Zn
Manganese	Required for fermentation of citrate by certain lactic acid bacteria, and with some milks the bacterial formation of diacetyl is inhibited by lack of sufficient Mn
Iodine	In the form of iodide ion; its concentration depends markedly on the amount consumed by the cow

The casein micelles contain undissolved calcium phosphate and a little citrate; it is often called "colloidal calcium phosphate".

Some cations (Ca^{2+} and Mg^{2+}) are associated with the negatively charged proteins. Small quantities of other ions (e.g. Cl^-) also may be bound to the proteins.

Almost all of the salt is in the serum or in the casein micelles, and very little is bound to the fat globules.

The salt in the casein micelles can be dissolved by lowering the pH to about 4.6 or lower and also, though slowly and incompletely, by dialysis against water or a calcium free solution.

DISTRIBUTION OF SOME SALTS BETWEEN CASEIN MICELLES AND SERUM

The phosphorus is present as orthophosphate, but part of it is bound to organic components like serine and threonine residues of casein, molecules of hexoses and glycerol, phospholipids, etc.

Phosphorus is also found in the hydroxyapatite structure of the colloidal calcium phosphate in the micellar structure of casein.

The sulfur content of milk is about 0.36 g per kg, but most of it is in the amino acid residues methionine and cysteine of the proteins. About 10% is present as inorganic sulfate.

The electrical conductivity is largely determined by the salt solution.

The presence of the proteins in milk does affect this pH, of course, as it affects the salt composition. The titratable acidity of milk depends both on its salt composition (largely phosphate content) and its protein content.

The freezing point of milk follows from the total concentration of dissolved substances especially chloride and lactose.

PHYSICAL EQUILIBRIA AMONG SALTS

Milk contains several elements but all of them are not entirely in a soluble state. Some minerals exist in colloidal and ionic state at the normal pH of milk. The compounds which are in soluble condition play an important role in keeping various milk constituents in stable condition. A balance exists between the components which are in soluble state and those which are in colloidal state.

SALT SOLUTION IN MILK

- ✓ The dissolved salts of milk are phosphate, citrate, chloride, sulphate, bicarbonate, sodium, potassium, magnesium and calcium.
- ✓ Physical equilibria among the milk salts for stability of milk is necessary, especially during heat processing. Colloidal particles of casein contain predominantly calcium, magnesium, phosphate and citrate. The chloride and sulfate are entirely present as the free ions Cl^- and SO_4^{2-} at the pH of milk.
- ✓ The salts of the various weak acids (phosphates, citrates and carbonates) are distributed among various ionic forms. Calcium and magnesium form complex soluble ions with citrate, phosphate (CaPO_4) and bicarbonates (CaHCO_3^+). The formation of such complex ions has the effect of reducing the concentration of calcium and magnesium ions in the solution.

SALT BALANCE IN MILK

- ✓ Salts in milk exist in colloidal and soluble form.
- ✓ A large amount of salt is present in casein micelles structure and is in equilibrium with salts in the soluble phase of milk.
- ✓ During acidification/fermentation of milk some salts gets solubilized from the colloidal state and come in to the soluble state. This destabilizes the casein micelle structure and tends to precipitate out as happens during curd setting of milk and preparation of acid casein.
- ✓ It also happens that the casein micelle stability is lost during heating of milk at high temperature such as in UHT processing, sterilization and boiling of milk. This is due to the in solubilization of colloidal calcium phosphate and final loss in the stability of milk, this in turn affects the quality of dairy products. Such changes in the salt balance also take place during manufacture of condensed milk, evaporated milk and milk powder.

SALT BALANCE IN MILK

The salt balance in milk is defined by the following equation

$$\text{Salt balance} = \frac{\text{Ca}^{+2} + \text{Mg}^{+2}}{\text{Citrate}^{-3} + \text{PO}_4^{-3}}$$

Balance between certain salts such as Ca^{+2} and Mg^{+2} with citrate and phosphate in the colloidal and soluble phase plays a pivotal role in the stability of casein micelles structure.

A delicate balance of cations and anions in the colloidal and soluble state is important in determining the stability of milk.

The monovalent cations (Na^{+}) have a dispersing effect, while divalent and trivalent cations (Ca^{+2} and Mg^{+2}) have an aggregating effect. Therefore, addition of sodium citrates and phosphate improves the heat stability of milk.

Colloidal salts remain in equilibrium with the dissolved salts.

Various treatments of milk may cause transfer of salts from one phase to the other.

Two-thirds of the calcium and one third of the magnesium and on half of the phosphorus are colloidal in normal milk. It is presumed that all the colloidal phosphorus is present in the micellar calcium phosphate.

A small portion of colloidal calcium is bound to α -lactalbumin. β -lactoglobulin can also bind calcium and magnesium and there is other minor calcium binding protein. Nearly all the sodium, potassium and chlorine are diffusible.

The principle dissolved salt constituents of milk consist of phosphate, citrate, chloride, sulphate, bicarbonate, sodium, potassium, magnesium and calcium.

At pH 6.6 of milk, sodium and potassium are not found in any combination with other constituents and are present as the cations Na^+ and K^+ while; the chloride and sulfate (salts of strong acids) are present as free ion Cl^- and SO_4^{2-} .

However, the salts of the weak acids (phosphate, citrates and carbonates) are distributed among various ionic forms. Calcium and magnesium form soluble complex ions with citrate, phosphate, and bicarbonates.

FACTORS AFFECTING SALT EQUILIBRIA

Temperature: The temperature will shift the balance among the various forms as milk is subjected to various cooling and heating treatments after it is drawn from the cow at 37 C. With the rise in the temperature the dissolved will be transferred to colloidal phase. Similarly, lowering the temperature below that at which the milk is drawn would cause a transfer of calcium and phosphate from the colloidal particles to the dissolved state.

Acidity: There will be pronounced shift in the salt equilibria with the addition of acid to milk whether directly or indirectly by bacterial action. Decrease in the pH withdraws the calcium and phosphate from colloidal particles until at about pH 5.2 all the calcium and phosphate is in the dissolved state.

Carbon dioxide content: Milk as secreted by the cow contains about 20 mg of CO₂ from milk is accelerated by heating and agitation. Removal of CO₂ would affect the balance in the rest of the system. It would be expected that the removal of CO₂ and the consequent rise in pH would be reflected in a shift in calcium phosphate from the dissolved to the colloidal state and probably also in a shift of calcium ions activity per 100 ml or about 10% by volume.

Concentration: As the milk is concentrated there is a tendency for calcium phosphate and calcium citrate to accumulate in the colloidal particles because the solubility is exceeded. As these materials are insolubilized, hydrogen ions are liberated, lowering the pH. The net result is an increase in concentration of citrate and phosphate in both the dissolved and colloidal state.

Sequestering agents and ionex changers: In order to stabilize the milk or even to improve the utility of milk for a particular purpose it is desirable to treat milk so as to alter its ionic balance. The best known example for this is the addition of phosphate or citrate to stabilize milk against subsequent heat coagulation. Addition of phosphate or citrate result in the binding of more of the calcium in the form of soluble complexes and decreasing activity of the calcium ions.