Unit IV – Topic I

Physical, Chemical, Thermal and Rheological properties of Milk

INTRODUCTION

Rheology is the study of the flow and deformation of matter. It is often used interchangeably with texture, which refers to the flow, deformation, and disintegration of a sample under force. In short, texture relates to solid foods, and viscosity - the tendency to resist flow - relates to fluid foods. Food can exhibit both solid and liquid characteristics, and rheology can identify the properties of such foods. Rheological studies are performed as a quality control method in dairy plants and as a technique for scientists to study the structure of the product.

Fluids will flow under the influence of forces, whereas solids will stretch, buckle or break. An ideal solid is represented by the Hooke solid, and the ideal liquid by the Newtonian liquid. Both are structureless (there are no atoms), isotropic (they have the same properties in all directions) and follow their respective laws exactly. Many materials can exert both types of properties, depending upon the environmental conditions and stresses they are subjected to. For example butter at 20 °C is regarded as a solid, although if the shearing force is sufficiently high, it can be made to flow or if its temperature is raised to above 50℃, it will melt and behave like a fluid.

Some of the rheological properties are also used for assessing and monitoring the quality of products such as cream, dahi, butter and cheese.

2.1.1 VISCOSITY

The dynamic viscosity μ is a parameter related to the inner friction of a liquid or fluid. It is reduced when temperature is increased. Due to the friction of the fat (emulsified in milk) and the dispersed protein, the viscosity of milk is twice as high as that of water. It increases with the protein coagulation and increasing fat content.

The dimension of the dynamic viscosity is Ns/m^2 or Pa-s; an old term is the centipoises cP (10^{-3} Pa-s). The value for milk at 5°C is a function of the fat content and ranges from 2.96 X 10^{-3} Pa-s (skimmed milk) and 3.25 X 10^{-3} Pa-s (whole milk); at 20°C we observe a range of 1.79 X 10^{-3} Pa-s and 2.13 X 10^{-3} Pa-s.

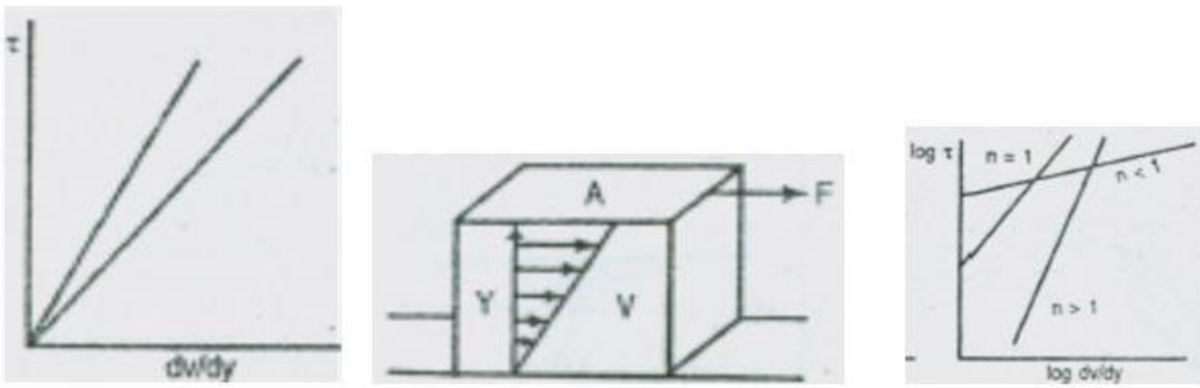
The viscosity of a fluid is the internal friction within the fluid. When a fluid is subjected to a shearing force (F) over a surface area (A), it will undergo a deformation known as flow (Fig. 2.1).

The shear stress is force/area. The rate of deformation termed as the shear rate is determined by the velocity gradient. For Newtonian fluids, there is a direct relationship between the shear stress (τ) and the rate of shear (dv/ dy). The ratio of the shear stress to shear rate is known as the dynamic viscosity or coefficient of viscosity (μ).

$$\mu = \tau/(dv/dy) = (\text{Shear stress}/\ \text{Shear rate}) = (Nm^{-2}/\ s^{-1}) = Nsm^{-2}$$

Viscosity data are often plotted as shear stress against shear rate, either in ordinary or logarithmic co-ordinates (Fig.2.l). Such plots are known as rheograms.

The two common units for viscosity measurements arc the poise (p) in cgs and the Poiseuille (PI) in SI. One Poiseuille is the dynamic viscosity of a fluid which, when subjected to a shear stress of 1 N m^{-2} gives a shear rate of 1 s^{-1}. The viscosity of water at 20℃ is 1.002 X 10^{-3} Nsm^{-2} or 1.002 cp.



(a) Deformation of a fluid

(b) Rheogram on ordinary co-ordinates

(c) Rheogram on logarithmic co-ordinates

Fig. 2.1 Deformation and rheograms of fluid

Milk, skim milk, cheese, whey and whey permeate are usually considered to be Newtonian fluids. The viscosity of all fluids is temperature dependent. The viscosity of liquids, pastes, suspensions and emulsions decrease with increase in temperature between 2-10 % for each℃. Therefore, it is important to control the temperature accurately when measuring the viscosity and temperature should always be quoted with the results.

Occasionally, it is more appropriate to the term kinematic viscosity which is dynamic viscosity/density. Kinematic viscosity is measured directly by the Ostwald capillary flow type viscometer. The viscosity of solutions increases as the concentration increases in a non-linear fashion. At high concentrations, small additional changes in the concentration will lead to rapid changes in the viscosity. This could result in reduced flow rates, higher pressure drops, decreased turbulence and severe fouling in heating operations. In concentration

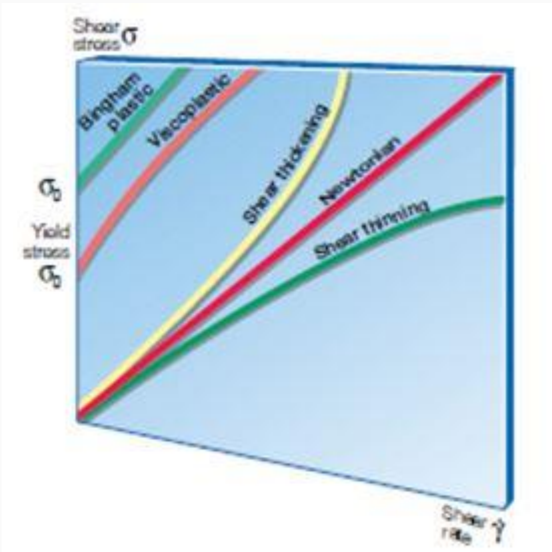
processes, the extent of concentration may well be limited by viscosity considerations. There is often a transition from Newtonian to non-Newtonian conditions as concentration proceeds.

Homogenisation and heat treatment both tend to increase the viscosity slightly, with homogenisation giving the milk a creamier mouth feel. The effect of homogenisation becomes more pronounced as the fat content increases.

The viscosity of milk products increases as the concentration increases. The viscosity of evaporated whole milk will depend upon the degree of forewarming, homogenisation conditions, the type of stabilizer used and the extent of the final temperature in-container heat treatment.

Viscosity is one of the main factors which limits the extent of concentration for ultrafiltration and reverse osmosis processes. The protein fraction makes the main contribution to the viscosity. Freshly separated cream has a fairly low viscosity. When cream is homogenised at fairly high pressures, usually after heat treatment, there is a significant increase in viscosity. Filling into cartons using piston filler will reduce the viscosity, probably due to shear breakdown but the viscosity then increases during cold storage. Cream cooled very quickly and stored at a uniform low temperature often shows a dilatant character.

Flow curves and viscosity curves for Newtonian and non-Newtonian fluids are shown in Fig.2.2 and Fig.2.3.



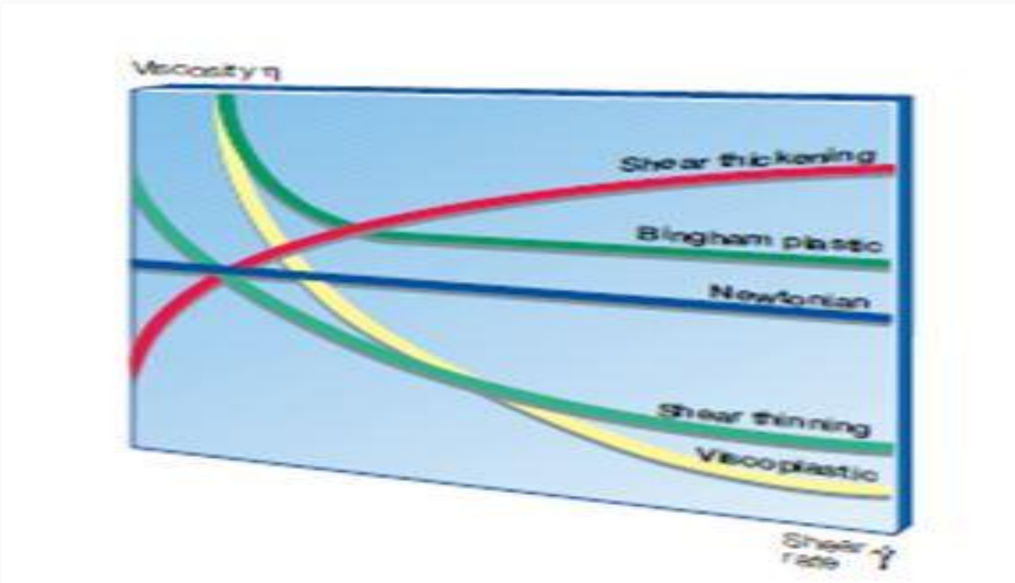
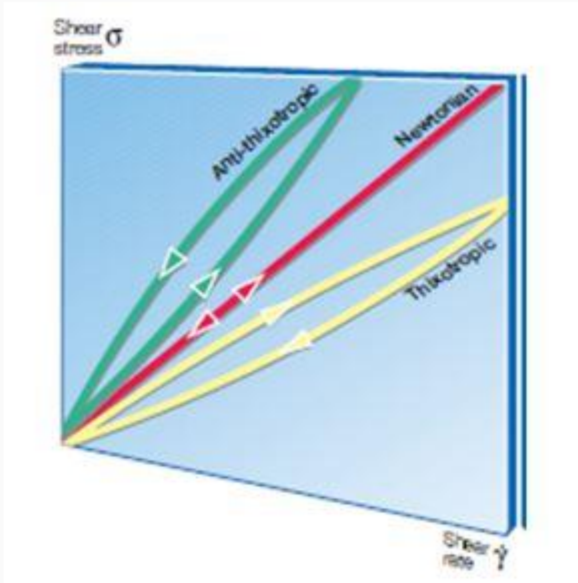


Fig. 2.2 Flow curves for Newtonian and non-Newtonian fluids Fig. 2.3 Viscosity curves for Newtonian and non-Newtonian fluids



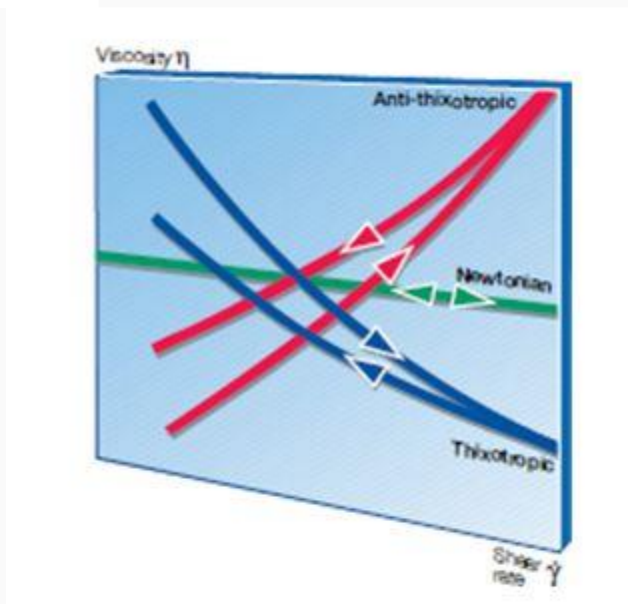


Fig. 2.4 Flow curves for time dependant non-Newtonian fluids Fig. 2.5 Viscosity curves for time dependant non-Newtonian fluids

2.1.2 Newtonian fluids

Newtonian fluids are those having a constant viscosity dependent on temperature but independent of the applied shear rate. One can also say that Newtonian fluids have direct proportionality between shear stress and shear rate in laminar flow.

A Newtonian fluid can therefore be defined by a single viscosity value at a specified temperature. Water, mineral and vegetable oils and pure sucrose solutions are examples of Newtonian fluids. Low-concentration liquids in general, such as whole milk and skimmilk, may for practical purposes be characterised as Newtonian fluids.

2.1.3 Non-Newtonian fluids

Materials which cannot be defined by a single viscosity value at a specified temperature are called non-Newtonian. The viscosity of these materials must always be stated together with a corresponding temperature and shear rate. If the shear rate is changed the viscosity will also change. Generally speaking, high concentration and low temperature induce or increase non-Newtonian behaviour.

Apart from being shear rate dependent, the viscosity of non-Newtonian fluids may also be time dependent, in which case the viscosity is a function not only of the magnitude of the shear rate but also of the duration and, in most cases, of the frequency of successive applications of shear. Non-Newtonian materials that are time independent are defined as shear thinning, shear thickening or plastic. Non-Newtonian materials that are time dependent are defined as thixotropic, rheopectic or anti-thixotropic. Flow curves and viscosity curves for time dependant non-Newtonian fluids are shown in Fig.2.4 and Fig.2.5.

Thermal properties of milk and milk products

3 INTRODUCTION

Milk and milk products undergo heating and cooling in dairy. Milk and other liquid foods are sometimes dehydrated to form powders. Cooling, cooking, baking, pasteurization, freezing and dehydration, all involve heat transfer. Design of such processes requires knowledge of the thermal properties of the materials involved. In this chapter, we will try to learn the thermal properties of milk and milk products.

3.1 Specific Heat

The specific heat is the amount of heat required to raise a unit mass through a unit temperature rise. The specific heat of most substances is slightly temperature dependent: this can be overcome by using an average specific heat value for the temperature range being considered.

The specific heat of milk usually ranges between 0.92 to 0.93 kcal $kg^{-1}C^{-1}$. Milk has highest specific heat (0.938 kcal $kg^{-1}C^{-1}$) at 15°C, however an average value of 0.93 kcal $kg^{-1}C^{-1}$ or 3.93 kJ $kg^{-1}K^{-1}$is used if temperature is not specified as

1 kJ $kg^{-1}K^{-1}$ = kcal $kg^{-1}C^{-1}$.

Relationship between the specific heat and temperature for fluid milk products is shown in figure no. 3.1.

The different components in foods have different specific heat values so it should be possible to estimate the specific heat of a food from knowledge of its composition. Water has the greatest influence on the specific heat.

$c = m_w c_w + m_s w_s$

where c = specific heat, m = mass fraction, water (w) and solids (s).

For dairy products consisting water (w), fat (f), and solids-not- fat (snf), the specific heat can be given as : .

$c = (0.5\ m_f + 0.3 m_{snf} + m_w)\ 4.18\ (kJ\ kg^{-1}\ K^{-1})$

Kessler (1981) has recommended the equation:

$c = 4.18\ m_w + 1.4\ m_c + 1.6\ m_p + 1.7\ m_f + 0.8\ m_a$

(water) (carbohydrate) (protein) (fat) (ash)

If the chemical composition is known, the specific heat can be estimated accurately. Values for frozen products can be obtained by substituting the specific heat of ice in the respective equations. This however assumes that all the water is in the frozen form.

The specific heat of milk concentrates in the temperature range 40-80℃ and total solids range (8 - 30%) can be calculated as:

$c = [m_w + (0.328 + 0.0027\ \theta)\ m_s]\ 4.18$

3.2 Specific heat capacity

The specific heat capacity c is the quantity of heat which is required to heat 1 kg of material by 1 K; the units are J/ kg OK (an old term is kcal/kg grad). 1 J/kg K = 2.389 X 10 kcal/kg grd. For water we have c = 4186.8, for all other materials c >4186.8 J/kg K. The specific heat content of milk depends on temperature and is lower at 40°C than at 15℃. The reason for this is that at 15℃ some fatty acids are still crystalline, so that additional heat is required for melting them.

Table 3.1 shows some values for c. Compared to milk, heating of butter requires only half as much heat. Values for the specific heat content are required for energy calculations for the thermal processing of milk (heating/cooling).

Table 3.1 Specific heat c

	Skim milk	Full cream milk	Cream 20 % fat	Butter
J/kg K	3977.5	3935.6	3516.9	2219.5

3.3 Latent Heat

Heat absorbed or released as the result of a phase change is called latent heat. There is no temperature change during a phase change, thus there is no change in the kinetic energy of the particles in the material. The energy released comes from the potential energy stored in the bonds between the particles. The major changes involved with dairy products are: the transition from water to ice (freezing), removal of water during evaporation and concentration, and the phase changes involved in the fat fraction when products are cooled below 50°C (crystallisation).

At atmospheric pressure, water boils at 100℃ and the latent heat of vaporisation is 2257 kJ kg-1. As the pressure is reduced, the boiling point decreases, and the latent heat value increases. At a pressure of 0.073 bar (absolute), the latent heat value is increased to 2407 kJ kg-l.

The latent heat of fusion for pure water is 335 kJ kg^{-1}. Unfortunately the situation for foods is more complex. The presence of solids depresses the freezing point, with most foods starting to freeze at about -10℃. This results in a concentration effect and a further depression of the freezing temperature. Therefore, the food does not freeze at a constant temperature: rather as freezing proceeds the temperature falls as most of the ice is converted to water: hence there is a concept of unfrozen water.

Most of the water freezes over the temperature range -1℃ to -100℃, and by -15°C, more than 90% of the water is frozen. The freezing point of milk is of considerable interest, because it is also used to detect any dilution of the milk. Most foods contain substantial quantities of solids, whereas only the water contributes to the latent heat value. On this basis, Lamb suggested the following equation to determine the latent heat value of food.

$L = m_w \times 335$ (kJ kg^{-1})

3.5 Thermal Diffusivity

The thermal diffusivity (k/ρc) is an extremely useful property in unsteady-state heat transfer problems; because it is a measure of how quickly temperature changes with time, during heating and cooling processes. It is extensively used in unsteady-state heat transfer problems in a dimensionless form known as the Fourier number

$F_o = at/r^2$

Where, t = heating time, a = thermal diffusivity, r= characteristic dimension of food.

Chemical properties of milk and milk products

4. INTRODUCTION

The physico-chemical properties of milk and milk products affect most of the unit operations used during their processing. These operations include fluid flow, heat transfer processes, mixing and churning, emulsification and homogenisation. Some of the rheological properties are also used for assessing and monitoring the quality of products such as cream. dahi, butter and cheese.

Raw milk is extremely variable in its composition and most dairy products can be produced in a variety of ways from this milk. There are two approaches to obtain, data for physical properties. The first is to use data available in the literature; the second is to determine the values experimentally.

4.1 DENSITY

Density is defined as the mass of substance divided by the volume occupied. Its unit in SI is the kilogram per cubic meter (kg m^{-3}). At 5°C water has a density of 1.00 g/ml or 10^3 kg m^{-3}.

The addition of solids, e.g. minerals, sugar, protein will increase the density, whereas oil and fat will decrease the density. The density of fluid is usually measured with a hydrometer. The density is temperature dependent, so temperature should always be recorded. The density of milk usually falls within the range of 1028 - 1035 kg m^{-3} depending on the composition. It is generally measured with a special hydrometer known as a lactometer and the result can be used to estimate total solids.

Boiling and Freezing Point

The boiling point for milk is 100.2℃, slightly higher than for pure water. The boiling point of both cow and buffalo milk ranges from 100.2℃ to 101℃ with an average of 100.5℃. The boiling point ranges slightly with the percentage of solids present in milk.

The freezing point of cow milk and buffalo milk ranges from – 0.535℃ to – 0.59℃ with an average of – 0.553℃ depending on the lactose, proteins and mineral content.

The average freezing point of raw milk is at -0.526℃; of pasteurized milk in the range -0.517 to -0.521℃. This is influenced (see also the boiling point) by the dissolved lactose and the similarly dissolved ions of the milk salt and a few other compounds with a relatively low molecular mass.

This relationship permits to detect adulteration with water or with additives e.g. salts, disinfectants or neutralizing agents.

The freezing point of raw milk has a lower value of -0.515℃, values of < -0.5℃ indicate adulteration with water. Values of > -0.62℃ indicate adulteration with salts.

The freezing point can be modified by gassing/ degassing of milk, lactose splitting or pH modification.

The presence of dissolved substances elevates the boiling point of a solution.

Dissolved substances lower the freezing point of a solution, since milk is a solution containing salts and sugars its freezing point is lower than that of water.

The fortification of milk with milk powder or lactose lowers the freezing point.