CHAPTER I
SECTION A
INTRODUCTION

Production and utilisation pattern of milk in India

India is essentially an agrarian country and a bulk of its national income is derived from agricultural products, a considerable portion of which, totalling to 7 per cent of the national income (N.I.C., 1984), originates from livestock resources. The total livestock population of the country in 1966 was 345.7 million (A.I.L.C., 1968). Out of this total 18.08 per cent consisted of cows and 7.42 per cent of the buffaloes. From the same report it is seen that the numbers of animals in lactation were 50.63 and 40.5 per cent of the total for the buffaloes and cows, respectively. In spite of this vast population of cows and buffaloes in milk the annual milk production of the country is very low and is insufficient to meet the nutritional requirement of the country. The latest available statistical informations put the annual milk production of India to 21,103 million tonnes (F.A.O., 1968). It could be further analysed that buffaloes contributed to 52.98 per cent of the total milk production of our country in comparison to that of 44.58 per cent by cows. In this respect India gives a different picture on comparison to world milk production. The total milk production of the world in 1967 (F.A.O., 1968) was estimated as 389,102 million tonnes. The cow population of the world contributed to 92.80 per cent of this total, while buffaloes contributed only to 4.85 per cent. Further, production of cow milk in India was 2.63 per cent of such
milk produced in the world, while Indian buffaloes contributed to 59.25 per cent of world's buffalo milk production in 1967. All these informations lead to the conclusion that under conditions buffalo milk is one of the important commodities of our country.

Milk from several animals have been considered as one of the most wholesome naturally occurring food all throughout the world since time immemorial. The people of India are traditionally milk conscious since long. The use of milk and ghee (clarified butter) obtained from milk has been mentioned in ancient Hindu scripture like Vedas. Utilization of milk for conversion into various other products like makhan (butter), matha (butter milk), dahi (curd), khoa (desiccated milk), etc., is prevalent throughout this country from scores of centuries past till these days. In addition to these traditional indigenous milk products, several others like whole and skimmed milk powder, condensed milk, ice cream and cheese, etc., have also being introduced during the last few decades from our contact with the western countries.

The rapid decomposition of untreated milk has been the principle motive to lead man to evolve methods for preserving some or most of its nutrients. Preservation of milk in one form or another is important for other reasons too. Unequal production of milk during different seasons of the year is one such reason. During summer and early rainy seasons there is usually a short supply of milk in India, while in other times of the year milk production is often more than enough
to cater the fluid consumption of the same (Ray, 1908) in many localities. Two important traditional methods of preserving and utilizing such surplus milk in India are churning milk into butter and subsequent conversion of the butter to ghee and partial dehydration of milk by heating on open pans to give the product variously called khoa, mawa, rabri, etc. A considerable portion of the surplus milk in our country is utilized for manufacture of ghee for various reasons. Milk is produced mostly in rural areas of the country. There are very few organised dairies to handle the milk produced in rural areas. For such, and other reasons, whatever surplus milk is available with the farmer producers, is mostly converted into ghee. Further, most of recently set up organised dairies in urban and semi-rural areas of the country are also utilizing surplus milk available in their locations for the manufacture of products like butter, cream and ghee. Analysis of the latest available statistics for utilisation of milk in India (Central Statistical Organisation, 1981) reveals that of the total milk produced in the country 45.23 per cent was utilised for fluid consumption, 31.85 per cent for ghee, 8.06 per cent for dahi, 6.37 per cent for butter, 4.74 per cent for khoa, 1.86 per cent for ice-cream, 1.19 per cent for channa and 0.70 per cent for cream production.

Milk concentrates and their importance

In the manufacture of ghee a large number of milk constituents and important nutrients are lost in the butter milk or skim milk, while in the preparation of khoa the drastic heat applied destroys to a considerable extent the
nutritional values of a good number of milk constituents. In contrast to these, manufacture of certain western products like evaporated milk, sweetened condensed milk, dried milk powder, etc., does not lead to an appreciable loss in most of the nutrients of the original milk (Kon, 1959). In particular, milk products of these categories are capable to provide proteins, calcium and a few vitamins which are badly needed for proper nutrition of Indian population. A few other advantages of condensed milk are narrated in the proceeding paragraph also. Manufacture of these products, particularly from available surplus milk, in India has not yet become common or appreciable in volume, as is evident from the statistics given in the earlier paragraph. During the recent past, however, some milk product factories organised in public, cooperative and private sectors are coming up. The approved capacity for these factories for various products are, expressed in tonnes per annum, whole milk powder 8258, skim milk powder 12910, infant food 19598, malted milk products 13458 and condensed milk 11059 (Souvenir, 1970).

In condensed milk almost all of the original constituents of milk are retained in small bulk. It has an added advantage of prolonged keeping ability, derived from its superior bacteriological quality obtained by either sterilisation in unsweetened condensed milk, often called evaporated milk, or addition of excess of sucrose in sweetened condensed milk. In its keeping quality condensed milk is superior to its indigenous counterpart, i.e., khoa, rabri, etc. Further, condensed milk can be reconstituted easily and thereby can
meet the demand to supply fluid milk during seasonal or local shortage. Owing to the light and flocculent nature of the curd and also to the smaller size of fat globules of such reconstituted milk, resembling those of human milk, it has easy digestibility. Consequently, it has recently got wide application in infant feeding programmes either as such or in combination with other nutritive substances like orange and tomato juice, lime and barley water, etc. Evaporated milk has its application in other food items like confectioneries, chocolate, sweetmeat and ice-cream mixes also.

Scope of the investigation

Notwithstanding such advantages of evaporated milk the problems involved in the manufacture and also in the storage of this product are many. Western workers, both manufacturer and researchers have encountered a number of such problems with evaporated milk manufactured from cow milk. Some such problems are gelation, protein denaturation and sedimentation, fat separation and browning of the products, developed either during manufacturing stages or on storage. Inspite of considerable research in many of these problems by several western research workers, a thorough understanding of the basic causes giving rise to the above problems or evaluation of foolproof techniques of manufacture of products free from these defects have not yet been achieved. A critical but brief review of studies for the problems mentioned above by a number of workers is likely to highlight the problems. Such a review has been attempted through a subsequent section of this chapter. Besides the same, a
few problems in utilisation of buffalo milk for the manufacture of condensed milk, anticipated or experienced by earlier workers, have also been presented. Further, a review to compare and contrast the composition as well as several important properties of buffalo and cow milks has been included in that section, since the same may help to disclose the specificity of the problems associated with processing of buffalo milk for concentrated milk products.

Examination of the various properties of buffalo milk in comparison to those of cow milk of Indian origin, as presented in the section to follow, indicates that there is considerable difference in the two milks with respect to some properties while in others there is hardly any. In its gross composition buffalo milk contains considerably higher proportion of fat as well as solids-not-fat. The total protein content and the lactose concentration, are also higher in buffalo milk. A difference exists in the mineral contents of the two milks, not only in quantity but in quality also, particularly in the nature of the "salt balance" and partitioning of the minerals between true and colloidal states of solutions. Of the physico-chemical properties crucial dissimilarity occurs in the heat stability, rennet coagulation time, make-up of the casein complex, densities of casein and fat and the pH.

An assessment of the problems associated with the manufacture of evaporated cow milk, focussed through several paragraphs under the "review of literature" (Section B, Chapter I), reveals that many of such problems have their origin in the possible interaction between the several milk
constituents, at least the major ones, like proteins, milk lipids, lactose and minerals. From the chemical standpoint, a study of such interaction between the major milk constituents is expected to yield valuable informations towards elucidation of problems associated with manufacture of evaporated milk, particularly the problems of coagulation during manufacture and gelation during storage. There are obviously a number of research tools which can be applied to study such problems. Each approach is likely to evaluate one or more particular nature of the problem and lead to partial solution of the same, although it may not solve the entire problem. Viscometry is one such research tool which can be applied advantageously to study problems associated with milk concentrates, particularly problems of heat coagulation and gelation in evaporated milk which are largely manifested in the viscous property of the product.

The complex physico-chemical nature of milk, presence of three phases of true solution, colloidal dispersion and emulsion, renders it quite difficult to study the interaction between milk constituents in situ. One of such difficulties is a limited scope of alteration, increase or decrease, in the concentrations of different milk constituents. Such alterations, however, are possible to be attained in model milk systems prepared from the milk constituents in variable proportions, so that such systems simulate milk of varying compositions. Study with model milk systems was made earlier by Clark (1927), Howat and Wright (1933), Tamman et al. (1957) and Muck and Tobias (1962), among others, to elucidate
several specific dairy chemistry problems. Considerable success in these studies has promoted to utilise this particular approach to elucidate viscometrically the possible interactions between major milk constituents and to utilise data therefrom in formulating optimum composition of buffalo milk suitable for the preparation of evaporated buffalo milk. Problems related to viscosity of evaporated buffalo milk are likely to be related to the pH of the original milk and its changes during processing. Practically no work in this aspect of the problem has been reported so far. Thus, simultaneous study of changes in the viscosity and pH of the model milk system and of milk during processing to evaporated milk is expected to throw light on problems associated with manufacture of evaporated buffalo milk.

Formation of sediment at the bottom, separation of fat at the top of containers on storage, appearance of deep colour usually called browning, and development of cooked flavour, either during manufacturing or on storage, are some defects which may develop in evaporated cow milk (Hunsiker, 1949; Hall and Hedrick, 1966). Observations towards the extent of development of these defects in evaporated buffalo milk have not been recorded so far either in India or elsewhere. The usefulness of a study yielding such data can hardly be overemphasized.

It is evident from a perusal of the contents of preceding paragraphs, and also from the literature review in Section B of this Chapter, that there is wide scope to study the several factors which may influence preparation and preservation of buffalo milk concentrates. In the
perspective of the state of production of milk and existing pattern of its utilisation, as presented briefly in the first few paragraphs of this chapter, it may not be too unrealistic to say that evolving a successful method for the manufacture of evaporated buffalo milk is a pressing problem to the dairyman in India. In view of the same a programme was undertaken to investigate the physico-chemical properties of model milk systems prepared with buffalo milk constituents, to utilise the findings therefrom in preparing evaporated buffalo milk on laboratory scale and to study the physico-chemical properties of such evaporated milk during preparation and preservation. A simultaneous study in the similar line involving cow milk constituents to gain knowledge of the behaviour of such constituents as compared to the same of those of buffalo milk was also made. The programme of work for these studies is outlined in Section C of this Chapter.
Problems in manufacture and preservation of evaporated cow milk

SECTION B
REVIEW OF LITERATURE

Gelation

The relative viscosity of concentrated milk product is one of the important attributes of good evaporated milk. The body of evaporated milk and also permanancy of the emulsion of fat in the milk is mainly controlled by the viscosity of the product. A full body product, having considerable high viscosity is desired by the consumer as it conveys an impression of richness and the food value of the product (Hunsiker, 1949). To the contrary, evaporated milk of low viscosity presents a thin body which may suggest to adulteration of the product and which may also lead to separation of the fat in the product, commonly called creaming off.

Changes in viscosity of milk take place to a different extent at different stages of manufacture. The viscosity of fresh milk does not change noticeably due to preheating of milk. The next stage of concentration (condensing) causes a slight but definite increase in viscosity. However, the final process of heating, that is, sterilization, applied to the concentrated milk increases viscosity of the product decisively (Mojonnier and Troy, 1922). Deyscher and coworker (1944) observed that viscosity of evaporated milk passes through well defined changes after sterilization and on storage. According to them first there was thickening during heat sterilization, then thinning on early storage and...
finally increase in viscosity on long storage leading to gel formation. The rapid thickening immediately preceding the visible coagulation was undoubtedly due to the process of coagulation. All milk samples did not, however, behave identically in this matter. The attainable body of a sample of evaporated milk at coagulation seemed to depend primarily upon the heat stability of the raw milk. Heat stability in its turn was largely influenced by the condition of forewarming, the concentration of milk solids and ionic equilibrium as existed in the milk serum. Further, they observed that viscosity attainable at coagulation and heat stability of the evaporated milk product were inversely related.

Tarassuk and Tamsma (1956) from their extensive study on control of gelation in evaporated milk concluded that gelation in stored evaporated milk was a problem of both theoretical and commercial importance. According to these authors also, gel formation in stored evaporated milk was not spontaneous, initially there was a thinning, (loss of viscosity), followed by a gradual thickening and ultimately complete immobilization of the fluid. Gelation was not accompanied by syneresis, and was clearly a different phenomenon from coagulation of milk by heat, rennet or other agents. Gel formation in evaporated milk was accelerated by storage at elevated temperature, and the same has also been concluded by Deysher et al (1944), Bell et al (1944), Simonson and Tarassuk (1952). Tarassuk and Tamsma further concluded that rate of gelation in evaporated milk on storage was a function of milk solids concentration and accelerated
rate of gelation with increased concentration was entirely associated with increase in concentration of the solids-not-fat fraction.

**Gelation and heat treatment**

The relationship between the speed and extent of gelation of evaporated milk on storage and time-temperature condition of forewarming of milk has been extensively studied by a large number of workers (Webb et al., 1943; Bell et al., 1944). The study of this problem, however, mostly has been associated to the study of effect of forewarming time and temperature on the heat stability of evaporated milk by a series of workers, namely, Webb and Holm (1928), Deysker et al. (1929), Welch and Doan (1935), Webb and Bell (1942), Bell and Webb (1943), Webb et al. (1943) and on milk by Davies (1959), Davies and White (1959), Hartman and Swanson (1962) and others. A common observation has been derived from such studies that marked variations in stability occur with changes in forewarming temperature and time. Rapid improvement in the heat stability of evaporated milk results with increasing forewarming temperature and associated shortening of forewarming time. Such improvement in heat stability of evaporated milk was, however, inversely proportional to storage stability as judged by the formation of a thin body of the product after sterilization followed by a rapid rate of its gelation on storing.

**Minerals, heat stability and gelation**

The role of minerals (salts) present in milk, in the heat stability of milk and evaporated milk has been
extensively studied since long. Pioneers in the field of such study are Sommer and his school of workers. Sommer and Hart (1919) observed that a critical balance between acidic and basic salt components of milk was necessary for maximum stability of milk to heat coagulation, besides other factors like the effect of albumin on the stability. In their opinion influence of other factors such as effect of acidity and that of heat treatment during the process of manufacture were dependent largely on their relation to salt balance in milk. Sommer and Hart (1922), Holm et al (1932) and Webb and Holm (1932) also studied the various aspects of heat coagulation of fresh and concentrated milks. The influence of milk minerals, mainly, calcium, magnesium, citrate, and phosphate has been established from their studies. The role of calcium and magnesium was further observed to be opposite to the that of citrate and phosphate. Sodium bicarbonate at higher concentration was also observed to exert an influence similar to that of citrate and phosphate to retard coagulation of evaporated milk. But at lower concentration this salt tended to hasten heat coagulation in evaporated milk, thereby behaving in the direction of calcium and magnesium ion. These workers further observed that in most cases coagulation was due to an excess of calcium and magnesium in the fluid milk. These observations and subsequent work (Sommer and Hart 1926) led to the development of the use of "addition and alteration" of salt concentrations in milk to achieve desired heat stability of milk during manufacture of evaporated milk. Such studies were extended further by Miller and Sommer (1940),
Cole and Tarassuk (1940), Maxcy and Sommer (1954), Harland et al. (1955), Humbert et al. (1956) and Verma and Sommer (1958a, 1958b). Heat stabilization effect of added salts although known and used in an empirical manner to give heat stable evaporated milk, has not been clearly understood yet. Near balancing of the total amounts of acidic and basic minerals in milk is not sufficient to render the milk stable towards heat; an excess of all acidic and basic constituents above normal quantity present in milk although maintaining their normal ratios may lead to heat instability (Rogers et al., 1921). The overall ionic equilibria in milk may be effective in controlling the degree of dispersion of proteins, while addition of stabilizing salts and heat treatments rendered to milk are likely to influence the ionic equilibria in milk (Kreveld and Minnen, 1955; Edmondson and Tarassuk, 1956; Verma and Sommer 1958a). The concentration of individual minerals present in milk and the mineral balance therefrom or from addition of either phosphate, citrate or calcium, magnesium, might be effecting heat stability of milk partially through their influence to change the pH of milk sample (Rose, 1961a, 1961b).

**Role of milk proteins on heat stability**

Rose (1962) further concluded that the influence of inorganic ions or salts on the heat stability of milk is possible only in the presence of $\beta$-lactoglobulin. The importance of $\beta$-lactoglobulin involving itself in complex interaction controlling heat stability of milk has been established by Rose (1961b, 1962). On the other hand crude
euglobulin and pseudoglobulin mixture (Rose 1901b) or 
α-lactalbumin fraction (Aschaffenburg and Drewry, 1957) did 
not contribute to the heat stability and pH relationship in 
milk. However, earlier accepted view of many workers 
(Davies, 1939; Pyne, 1958; White and Davies, 1958; Pyne, 1962) 
was that the presence of albumin and globulin was not related 
to heat stability of the milk unless their concentration 
exceeded 0.9 per cent. The definite role of β-lactoglobulin 
in heat stability of milk has been explained to its heat 
denaturation in the presence of casein and likely association 
of this protein with K-casein component of later (Tilley, 
1960; Morr et al, 1962). Rose (1965) further stressed on 
the great influence of K-casein-β-lactoglobulin complex 
formation, has on the heat stability of milk. Various other 
conditions like pH, salt concentration and surface condition 
of casein micelles, etc., however, were supposed to be 
controlling factors of the influence of β-lactoglobulin on 
heat stability of milk.

The influence of overall protein content in milk on 
the viscous property of evaporated milk prepared and on the 
tendency towards gelation of the same has been studied by 
Beeby and Loftus Hill (1966). The study primarily involving 
the role of the breed of cow on the gelation of evaporated 
milk revealed that milk from cows of certain breed like 
Jersey containing greater protein to water ratio yielded 
evaporated milk more prone to gelation. These workers 
suggested standardization of evaporated milk to an optimum 
protein content, in addition to the same for fat and solids-not-fat content.
Tarassuk and Simonson (1951) from their study on the gel formation and fat separation in evaporated milk effected by the state of milk protein attempted to explain gel formation in evaporated milk on the basis of physical and chemical changes brought about by slight hydrolysis of milk proteins. Changes in shape of protein molecules from spherical to linear type and the increase in the number of polar groups were also considered to be taking place leading to increased hydration of the proteins and its influence on the body of evaporated milk. Corradini et al. (1967) reported that sediment formation was a first step towards gelation in evaporated milk. They, however, considered that the action of steam injection in the process of manufacture on \( \beta \)-lactoglobulin in milk was in some way responsible for gelation. Hostettler and Imhof (1963) by studying the structural changes in casein by viscometry also supported the above observations and showed that these defects can be avoided by reversing the order of treatment i.e., by employing steam injection before homogenization.

Changes in the nature of the casein particles as observed by electron microscopy in sterile concentrated skim milk and its relation to the development of gelation were studied by Schmidt (1968), Schmidt and Buchheim (1968) and Schmidt (1969). It has been observed that in the conventionally sterilized (13 minutes, 118°C) concentrated milk the general appearance of the casein particles did not vary much during storage for six months at 28°C. In UHTST sterilized (15 seconds, 135°C) concentrated milk casein particles
started to coalesce immediately before the milk solidified completely due to age thickening. These workers further observed that addition of orthophosphate increased such agglomeration of casein particles while addition of polyphosphate prior to sterilization did not lead to agglomeration.

**Fat separation on storage**

Heat and storage stability of evaporated milk are often affected by the lipid phase of milk. A definite tendency of objectionable fat separation during age thinning and before age thickening commencement has been encountered in the storage of evaporated milk (Deysher et al. 1944; Hunsiker, 1949; Webb et al. 1951; Tamsma and Tarassuk, 1956). The introduction of HTST sterilization of concentrated milk in the manufacture of evaporated milk has led to an aggravation of the problem of fat separation on storage (Bell et al. 1944; Simonson and Tarassuk, 1952; Leviton and Pallansch, 1961b). The work of Leviton and Pallansch on the role of lipid phase on both heat and storage stability of HTST evaporated milk has shown that fat phase undoubtedly participates in the coagulation process in evaporated milk. According to these authors fat phase bears a quasi-inert nature which has two contradictory functions - one favouring the coagulation process, other hindering it; the fat particles in the former case behaving as the proteins and in the later case as a truly inert emulsoid. Maxey and Sommer (1954) studying the phenomenon of fat separation in evaporated milk have discussed the various causes for the phenomenon and remedial measures, such as, effective homogenization with respect to the temperature and condition
Browning of evaporated milk

One of the problems encountered with evaporated milk is its tendency to develop a deeper colour from the usual opalescent white of milk and the same is known as browning. Webb and Holm (1930), and Webb (1935) from their pioneering studies on the problem observed, beside other, that traces of copper and iron salts promote browning while tin salts inhibited the same. Sodium bicarbonate used as neutraliser darken the colour in proportion to the amount added but sodium phosphate did not produce the browning. However, heat treatment during forewarming and sterilisation were the most important factor leading to browning in evaporated milk (Webb and Holm, 1930; Bell and Webb, 1943; Bell et al., 1944; Nelson, 1945; Simonson and Tarassuk, 1952; Tarassuk and Simonson, 1950). The development of browning has been observed (Bell, et al., 1944; Tarassuk and Simonson, 1950; Simonson and Tarassuk, 1952) to be more in evaporated milk subjected to the conventional heat treatments i.e., lower temperature long time heating for forewarming, and, more so, far sterilisation. If the HTST process was used for forewarming and sterilisation the evaporated milk formed was essentially free from browning. Such HTST product, however, had its other defects, such as, thinning and subsequent gelation on storing, as has been mentioned earlier. Many other factors like alkaline stabilising salt, high solid content, head space oxygen in the can (Tarassuk, 1947), pH of milk and some unknown characteristics of raw milk (Webb and Holm, 1930; Bell and Webb, 1943) are also responsible.
for formation of browning.

The temperature of storage as well as length of storage period have their influence on the development of browning (Webb and Holm, 1930; Tarassuk and Simonson, 1950; Webb et al., 1951; Patton, 1952). Low temperature of storage, 0°-5°C, was found to prevent the development of browning while browning proceeded with increased temperature and time of storage.

Problems in utilisation of buffalo milk for manufacturing evaporated milk

The foregoing review of literature was concerned with the problems of preparation of evaporated milk from cow milk in Western countries under a climatic condition different from that prevalent in India. Similar information on the problems of preparation of evaporated buffalo milk are very scanty. Some of the problems presented by various workers are discussed below.

Davies (1941) while stating "there was no knowledge of the behaviour of buffalo milk in the condensing process" suggested that the concentration ratio at least will be less than Western milk. He further pointed out that composition of buffalo milk would have to be standardised, acidity would have to be corrected, preferably by method which would also increase the heat stability of milk proteins, and protein stability in sterilisation process for evaporated buffalo milk would have to be investigated.

Anantakrishnan and Kothavalla (1947) recommended toning of buffalo milk to 4 per cent fat by the addition of buffalo skim milk to get a condensed product. They also
recommended the addition of stabilisers, disodium hydrogen phosphate (36 mg per 100 g of evaporated milk) and sodium citrate (48 mg per 100 g of evaporated), to increase the heat stability of buffalo milk during the preparation of evaporated milk. They further observed that addition of bicarbonate at a concentration of 48 mg per 100 g of evaporated milk gave good heat stability to all evaporated milk samples, but led to development of brown colour. These workers also concluded that temperature of coagulation of evaporated milk during 30 minutes' sterilization decreased progressively with increased concentration of total milk solids, and forewarming of the milk at 203°F (95°C) for 5 minutes gave maximum heat stability during sterilization.

Dudani and Iya (1963) reported that difficulty was encountered in the manufacture of buffalo evaporated milk in obtaining a concentration of more than 26 per cent total solids in the finished product. They further mentioned the following as other problems, separation of fat, browning of the product, and gel formation of evaporated milk during certain season of the year at sterilisation temperature used. According to them, some of these difficulties were due to the differences in salt balance in buffalo milk from those of cow milk.

Godbersen (1964) while discussing the utilisation of buffalo milk for modern dairy products mentioned that recorded difficulties in making dairy preserves from buffalo milk are denaturation of proteins, observed as a change in texture and body towards crumbliness, and fat leaking. He, further,
suggested that gelation of evaporated milk was connected with browning, discolouration, and burnt flavour. Another problem with buffalo milk was stated to be lesser heat stability of condensed and dried milk products.

Srinivasan et al. (1967) stated that "evaporated milk has not so far been commercially produced within the country. There are reports of the failure of initial attempts to make this product using buffalo's milk which, owing to low heat stability, does not lend itself to initial concentration and subsequent high temperature sterilisation".

**Difference in the composition of buffalo and cow milks**

The problems discussed in the references mentioned through the previous paragraphs are mostly concerned with the manufacturing conditions of evaporated buffalo milk following the techniques and equipments used by Western workers handling cow milk as raw material.

A considerable difference in the composition of buffalo and cow milks with respect to some major milk constituents and also to the gross composition are known since long. Further studies during the last few decades have revealed considerable differences in a number of properties in milk from the two species. Such differences are likely to reflect on the specificity of problems involved in the preparation of buffalo milk concentrates. A brief review of the same is, therefore, attempted through the paragraphs following.

**Gross composition**

Differences in specific gravity, in gross composition
and in concentrations of some major milk constituents are presented, for the sake of ready comparison and saving of space, in Table A following, which is self explanatory. The data have been collected from different sources as described hereafter, their serial numbers agreeing with the reference numbers in column 1 of the Table A.

1 Maggit and Mann (1911, 1912)
2 Smith (1925, 1928)
3 Bunce (1932)
4 Schneider et al (1948)
5 Amble and Jacob (1960)
6 Basu et al (1962)
7 Ghosh and Anantakrishnan (1965)

**Protein components**

Ghosh and Anantakrishnan (1965) while studying the relationship between the milk constituents reported average casein content of buffalo milk 3.155 per cent as compared to 2.56 per cent for the cow milk. Likewise average albumin contents were 0.342 and 0.258 per cent for buffalo and cow milks, respectively, while corresponding values for globulin per cent were 0.170 and 0.188. These workers further presented the percentage of proteose peptone in buffalo milk as 0.156 and in cow milk as 0.130; whereas the non-protein nitrogen content of buffalo milk was 0.216 per cent and that of cow milk 0.176 per cent. These authors also observed that there was a positive and significant correlation between
Table A
Comparison of the specific gravity and gross composition of milks from Indian buffalo and cattle

<table>
<thead>
<tr>
<th>Ref. No. &amp; Year</th>
<th>Breed</th>
<th>Specific gravity</th>
<th>Total solids</th>
<th>Solids (Not-fat)</th>
<th>Total Fat</th>
<th>proteins</th>
<th>Lactose</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1911</td>
<td>Buff.</td>
<td>1.0291</td>
<td>13.32</td>
<td>4.05</td>
<td>7.12</td>
<td>10.66</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cow</td>
<td>1.0301</td>
<td>13.32</td>
<td>4.05</td>
<td>7.12</td>
<td>10.66</td>
<td>0.75</td>
</tr>
<tr>
<td>2</td>
<td>1925</td>
<td>Buff.</td>
<td>1.0291</td>
<td>13.32</td>
<td>4.05</td>
<td>7.12</td>
<td>10.66</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cow</td>
<td>1.0301</td>
<td>13.32</td>
<td>4.05</td>
<td>7.12</td>
<td>10.66</td>
<td>0.75</td>
</tr>
<tr>
<td>3</td>
<td>1932</td>
<td>Buff.</td>
<td>1.03143</td>
<td>15.75</td>
<td>9.19</td>
<td>6.56</td>
<td>3.86</td>
<td>5.23</td>
</tr>
<tr>
<td>4</td>
<td>1948</td>
<td>Buff.</td>
<td>1.0324</td>
<td>15.75</td>
<td>9.19</td>
<td>6.56</td>
<td>3.86</td>
<td>5.23</td>
</tr>
<tr>
<td>5</td>
<td>1960</td>
<td>Buff.</td>
<td>1.0324</td>
<td>18.58</td>
<td>8.19</td>
<td>5.70</td>
<td>4.90</td>
<td>3.43</td>
</tr>
<tr>
<td>6</td>
<td>1962</td>
<td>Buff.</td>
<td>1.02903 to 1.0324</td>
<td>15.75</td>
<td>9.19</td>
<td>6.56</td>
<td>3.86</td>
<td>5.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cow</td>
<td>1.02903 to 1.03066</td>
<td>13.449</td>
<td>8.460</td>
<td>4.968</td>
<td>3.178</td>
<td>4.88</td>
</tr>
<tr>
<td>7</td>
<td>1965</td>
<td>Buff.</td>
<td>1.02903 to 1.0324</td>
<td>15.75</td>
<td>9.19</td>
<td>6.56</td>
<td>3.86</td>
<td>5.23</td>
</tr>
</tbody>
</table>

Buff. = Buffalo
M = Morning milk sample
E = Evening milk sample
* Value under lactose is for the total for lactose and ash.
casein and albumin, and a positive but not-significant correlation between casein and globulin, a negative and not-significant correlation between casein and non-protein nitrogen of both buffalo and cow milks. Further, the correlation between casein and proteose peptone although positive in both the cases of cow and buffalo milks was significant in the former case only.

Ganguli and Bhalerao (1964) reported the respective concentrations of $\alpha^\prime$, $\beta^\prime$, $\gamma^\prime$ fractions of casein as 44.5, 52.4 and 3.1 per cent of whole casein in buffalo milk casein and 54.5, 39.1 and 6.4 per cent in cow milk casein. Singhal and Ganguli (1965) observed that these three components of casein from buffalo milk had slower electrophoretic mobility as compared to those from cow milk.

**Mineral composition**

In general, buffalo milk contains higher proportion of the individual minerals, excepting those of chloride and citric acid. The individual mineral constituents of buffalo milk have been studied by several workers and a few representative results are cited below.

**Calcium**

The average calcium content of buffalo and cow milks was reported by Anantakrishnan et al. (1943) as 0.163 and 0.127 per cent, respectively. Verma and Anantakrishnan (1946) while reporting average content of total calcium in buffalo herd milk 0.131 per cent and in cow herd milk 0.153 per cent studied further partitioning of calcium between soluble and
collodial states. They observed that in buffalo milk 77.49 per cent of the total calcium was in the casein bound colloidal form, but in cow milk such calcium was only 67.09 per cent. Basu et al (1962) from their study of composition of milk and ghee obtained the average calcium content for Murrah buffalo herd milk 0.1747 g/100 ml; similar value for cow herd milk ranged between 0.1420 to 0.1632 g/100 ml from milks of Red Singhi, Gir, Sahiwal, Tharparkar and Cross-bred cattle. Schneider et al (1948) reported ionic calcium content of buffalo milk 0.185 per cent as compared to that of cow milk 0.146 per cent.

Magnesium

The magnesium content of either buffalo milk or cow milk of Indian origin has not been studied so extensively. Anantakrishnan et al (1943) reported 0.013 per cent Mg in buffalo milk and 0.014 per cent in cow milk. Acharya and Devadatta (1939) observed magnesium concentration of 15.36 mg in soluble form and 2.46 mg in insoluble form in 100 ml of buffalo milk.

Phosphorus

Acharya and Devadatta (1939) in their study on distribution of calcium, magnesium and phosphorus in buffalo milk from Bombay reported 0.083 per cent phosphorus in buffalo milk. Basu and Mukerjee (1943) obtained 125.3 mg of total

* These workers presented their results as per cent CaO, and also per cent P2O5, to be reported subsequently, from which the above values were calculated.
phosphorus in 100 ml of buffalo milk, and 97.6 mg of the same in 100 ml of cow milk. Anantakrishnan et al. (1943) observed a comparatively lower phosphorus content in buffalo milk, 0.101 per cent, while the same in cow milk was 0.092 per cent. Schneider et al. (1948) from their extensive analysis of buffalo and cow milk samples from Allahabad, obtained the total phosphorus content of buffalo milk 0.121 g/100 ml, while that of cow milk 0.099 g/100 ml. Basu et al. (1962) reported the total phosphorus of buffalo milk from Murrah herd 0.117 per cent. The total phosphorus content in cow milk obtained from herd of five breeds, Red Sindhi, Gir, Tharparkar, Sahiwal and Cross-bred animals, ranged from 0.101 to 0.112 per cent. Sengupta and Chanda (1959) mentioned that buffalo milk has more ester phosphorus and less phosphate than cow milk.

Citric acid

Anantakrishnan et al. (1943) reported the citric acid content of buffalo milk 0.196 per cent and that of cow milk 0.255 per cent. Basu et al. (1962) gave the concentrations of acid 0.1813 per cent in buffalo milk; the same ranged from 0.1837 to 0.2084 per cent in milk from five breeds of cow. It is seen from these results that buffalo milk contains less citric acid as compared to cow milk.

Chloride

All the results for chloride content of milks from Indian buffalo and cow reported by a number of workers (Sen and Dastur, 1947; Schneider et al., 1948; Praphulla and Anantakrishnan, 1958; Singh et al., 1961; Basu et al., 1962),
although varying widely in actual values, clearly indicated that buffalo milk contained less chloride than cow milk.

Through the previous paragraphs an attempt has been made to express the differences present in gross composition and in concentrations of some major constituents of buffalo and cow milks. Considerable differences in the content of some minor constituents, like trace elements, carbon dioxide, vitamins, colouring matters and enzymes, etc., have also been reported by several workers, as can be observed from the review of such data by Dastur (1956), and by Laxminaraya and Dastur (1968).

Differences in the physico-chemical properties of buffalo and cow milks

Density of milk and milk constituents

The density of buffalo and cow milks expressed in terms of specific gravity has been presented earlier in Table A.

Density of casein dispersed in form of sodium caseinate at pH 7.0 and at 30°C was 1.325 and 1.383 g/ml for buffalo and cow milk caseins, respectively. The density of micellar casein was, however, comparatively higher, 1.422 and 1.456 g/ml respectively for buffalo and cow milk caseins at 30°C and 7.0 pH (Roy, 1968). Density of buffalo milk fat has been observed to be significantly higher than that of cow milk fat, 0.9084 and 0.9012 g/ml at 30°C for buffalo and cow milk, respectively (Dixit, 1969).

Size of fat globules

Size and distribution of fat globule in milk of two species, buffalo and cow were found to differ. Kothavalla
and Sunawalla (1937) reported average diameter of fat globules in buffalo milk to vary from 5.4 to 5.7 μ depending on breed, while the average diameter of fat globules in cow milk from different breeds of animal ranged between 2.9 and 3.7 μ. Puri et al. (1952), however, observed average diameter of milk fat globules to range from 4.05 to 4.80 μ in buffalo milk and from 3.59 to 4.0 μ in cow milk.

Shape of casein micelles

From a viscometric study of dilute casein solutions, Roy and Bhalerao (1966) determined the axial ratios and also the volume fractions of the dissolved casein molecules. They observed that the axial ratio of buffalo milk casein was 12.92 and that for cow milk casein 13.72 at pH 7.0 and 30°C. Besides the more elongated shape of cow milk casein, a lesser casein-solvent interaction was also observed in cow milk casein in comparison to that in buffalo milk casein.

Acidity, pH and buffer value

Gulvady (1952) observed a range of 0.12 to 0.13 per cent for acidity of milk from Murrah buffaloes. In comparison, the acidity varied from 0.13 to 0.14 per cent for milk from cows of five breeds, Red Sindhi, Sahiwal, Tharparkar, Gir and Cross-bred. Significant positive correlations between acidity and fat and between acidity and solids-not-fat in buffalo milk but an absence of such correlation in cow milk was observed by Bhimsena Rao and Dastur (1955).

A significant negative correlation between pH and acidity in buffalo milk and an absence of such relation in
Cow milk was observed by Bhimsena Rao and Dastur (1955, 1956b). In these studies these authors recorded an average pH of 6.74 in milk from Murrah buffalo. In milk from cow of different breeds the pH ranged from 6.60 to 6.64. Further, this difference in pH of milk from two species was found to be highly significant. The maximum buffer value was observed by Bhimsena Rao and Dastur (1956a) as 0.0417 at pH 4.90 – 5.00 in buffalo milk and 0.0359 at pH 5.1 – 5.2 in cow milk. In consonance to the higher buffer value in buffalo milk, this milk was observed to develop acidity more slowly than cow milk under identical condition of storage and in the initial stages of storage (Bhimsena Rao and Dastur 1956a).

Viscosity and curd tension

Viscosity of buffalo milk was observed to be higher than that of cows milk (Puri and Gupta 1955). Kulkarni and Dole (1956) from their detailed study reported average viscosity at 30°C as 17.73 millipoise for buffalo milk and 15.76 millipoise for cow milk. These workers observed increasing viscosity with increase in the size of fat globules.

Rao et al (1964) studied the curd tension of milk from buffalo and cow and reported that the milk from the former had a curd tension 1.5 times more than that of later.

Freezing point

The freezing points of buffalo and cow milks although extensively studied by several Indian workers have not shown a regular trend. Some workers (Macmohan and Srivastava, 1935; Puri and Parkash, 1961) observed higher freezing point of
buffalo milk than that of cow milk, e.g., -0.5454 and -0.5408°C for the above two milks, respectively (data of Puri and coworker). Others (Schneider et al., 1948; Dharmarajan et al., 1950, 1953, 1954; Dastur et al., 1952) recorded slightly lower freezing point for buffalo milk as compared to that for cow milk, for example, -0.5426 and -0.5455°C for the former and latter milks, respectively (data of Schneider et al.). Yet a third group (Sen and Dastur, 1947) reported overlapping values, -0.549°C for buffalo milk and -0.548, -0.549, -0.547, -0.544 and -0.548°C for cow milks from cattle of respective breeds of Red Sindhi, Gir, Tharparkar, Sahiwal and Cross-bred. It can be mentioned in passing that some Egyptian workers (Hof i et al., 1968a) observed freezing point depression for buffalo milk to be significantly lower than that for cow milk.

Electrical conductance

The electrical conductivity of buffalo milk has been controversially reported. Puri and Parkash (1963a) observed slightly higher value for electric conductance for buffalo milk than that for cow milk, namely, 6.690 ± 0.223 and 6.615 ± 0.271 millimhos at 25°C for buffalo and cow milks, respectively. Pal (1963), however, recorded from an average of 3 observations the electrical conductivity of buffalo milk 32.17 x 10⁻⁴ mhos and for cow milk 44.00 x 10⁻⁴ mhos (temperature not mentioned).

Rennet coagulation

Buffalo milk was observed to take less time to
coagulate with rennet than did cow milk (Sen and Dastur, 1947). Using 50 ml of milk at 37°C and adding one ml of 10 per cent. Hensen’s liquid rennet, they observed the average rennet coagulating time for buffalo milk, for over 2,000 observations, was 39.5 seconds in the range of 31.52 to 53.0 seconds; the corresponding values for cow milk were 45 seconds and 31.52 to 35.0 seconds. Krishnamurti and Subrahmanyan (1948) also confirmed the observations of Sen and Dastur. Puri and Parkash (1962) using 50 mg of powdered Hensen’s rennet for 100 ml of milk at 15°C observed a maximum coagulation time upto 66 minutes for buffalo milk while a maximum of 406 minutes for cow milk. Sharma and Bhalerao (1964) reported the average rennet coagulation time (for 25 samples) for buffalo milk at 30°C to be 1.15 in the range of 0.75 to 1.54 minutes; the corresponding figures for cow milk were 51.5 and 23.77 to 72.64 minutes.

Alcohol test

Buffalo milk has been reported to be less stable than cow milk under the influence of alcohol. Gajraj Singh et al (1947) have observed that concentration of alcohol generally used in the case of cows milk was too strong for buffalo milk to reach the same end point. Minib (1958) observed that concentrations of calcium and magnesium in buffalo milk was usually very close to the critical level to give a positive alcohol test. Addition of 5-10 mg of calcium per 100 ml of raw buffalo milk was enough to give an alcohol test positive, but in the case of cow milk 20 - 25 mg per 100 ml was required for the same. Puri et al (1965) also confirmed that buffalo
milk was less stable than cow milk under the influence of alcohol.

Heat stability

There is very little published report on the nature of heat stability of buffalo milk. Puri and Parkash (1963b) observed that average heat coagulation time for buffalo milk varied from 195.1 minutes at 110°C to 93.6 minutes at 140°C. For cow milk the same varied from 124.0 to 59.4 minutes corresponding to these two temperatures. The coagulation time for buffalo milk at 130°C was in the average of 106.2 minutes. Although there is no other published reference for heat coagulation time of milk from Indian buffalo, such results for Egyptian buffalo milk (Abd El-Salam 1968) show a wide difference. According to the later worker, the average heat coagulation time for buffalo milk at 130°C was only 21.6 ± 1.63 and 23.1 ± 1.20 minutes for bulk and individual samples, respectively; the same for milk from Western breed cattle varied from 17.2 to 59.0 minutes for herd samples and 0.6 to 86.2 minutes for individual samples (White and Davies, 1958). Such results indicated that buffalo milk (Egyptian) was slightly less stable than cow milk towards heat. The results of Puri and Parkash (1963), however, are contradictory to the same.
The present research project was divided into three phases, described under the following headings:

I. Investigation into physico-chemical properties of model milk system.

II. Preparation of evaporated milk in laboratory scale and study of its physico-chemical properties.

III. Study of changes in the physico-chemical properties of evaporated milk on storage.

I. Investigation into physico-chemical properties of model milk systems

1. Preparation of model milk systems using both buffalo milk casein and cow milk casein in varying proportions; study of change in viscosity and pH of such systems.

2. Preparation of model milk systems with different concentrations of both casein and lactose and study of change in viscosity and pH of such systems.

3. Preparation of model milk systems with definite concentrations of casein and lactose but varying concentrations of
   (a) major milk minerals, namely, calcium, magnesium, phosphate, citrate and chloride,
   (b) total whey proteins, \( \alpha \)-lactalbumin and \( \beta \)-lactoglobulin fractions of whey proteins,
   (c) milk lipids.

Also study of change in viscosity and pH of such model milk systems under different conditions of heating and storage.
4 Preparation of model milk systems having different concentrations of total milk solids with all the above mentioned major milk constituents and study of the prior mentioned physico-chemical properties of such systems.

II. Preparation of evaporated milk in laboratory scale and study of its physico-chemical properties

1 Preparation of evaporated buffalo milk in laboratory scale under the following conditions:
   a) Standardisation of fat content of raw milk.
   b) Incorporation of casein.
   c) Incorporation of minerals.
   d) Forewarming.
   e) Condensation in the ratio of milk 2:1 for total milk solids.
   f) Homogenization.
   g) Sterilization and aseptic sealing of the product for storage.

2 Study of changes in viscosity and pH of fat-standardized milk and of the products subsequent to each processing steps.

3 Preparation of evaporated cow milk under the conditions mentioned above for buffalo milk excepting without standardising raw milk for fat and with concentration in the ratio of 2.3:1 for total milk solids. Subsequent study of earlier mentioned physico-chemical properties.
III. Study of changes in the physico-chemical properties of evaporated milk on storage

1 Study of evaporated milk at controlled low and high temperatures for periods up to six months.

2 Study of the changes in the following physico-chemical properties of evaporated milk samples due to storage with a view to assess the keeping quality of the same:
   a) Viscosity.
   b) pH.
   c) Browning.
   d) Sedimentation.
   e) Fat separation.
   f) Flavour.

3 Reconstitution and study of viscosity and pH of reconstituted milk.

4 Bacteriological quality of evaporated milk prepared and subsequent to storage.

The material used and several experimental procedures followed to make the above outlined investigation are described in details in Chapter II. The results of all such studies are presented in Chapter III and those are critically discussed in Chapter IV. The summary of results including pertinent conclusions derived from above studies are presented in Chapter V. A list of references cited in the text of all the chapters follows Chapter V.