REVIEW ARTICLE

Casein micelle structure: a concise review

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Abstract

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Milk is a complex biological fluid with high amount of proteins, lipid and minerals. The function of milk is to supply nutrients such as essential amino acids required for the growth of the newborn. In addition, due to the importance of casein and casein micelles for the functional behavior of dairy products, the nature and structure of casein micelles have been studied extensively. However, the exact structure of casein micelles is still under debate. Various models for casein micelle structure have been proposed. Most of the proposed models fall into three general categories, which are: coat-core, subunit (sub-micelles), and internal structure models. The coat-core models, proposed by Waugh and Nobel in 1965, Payens in 1966, Parry and Carroll in 1969, and Paquin and co-workers in 1987, describe the micelle as an aggregate of caseins with outer layer differing in composition form the interior, and the structure of the inner part is not accurately identified. The sub-micelle models, proposed by Morr in 1967, Slattery and Evard in 1973, Schmidt in 1980, Walstra in 1984, and Ono and Obata in 1989, is considered to be composed of roughly spherical uniform subunits. The last models, the internal structure models, which were proposed by Rose in 1969, Garnier and Ribadeau-Dumas in 1970, Holt in 1992, and Horne in 1998, specify the mode of aggregation of the different caseins.

Key words : casein micelle structure, casein micelle models, casein coat-core structure, casein sub-micelle, internal structure model of casein

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บทคัดย่อ

ชนกภัทร ผดุงอรรถ

โครงสร้างของเคซีนไมเซลล์

ว. สงขลานครินทร์ วทท. 2548 27(1) : 201-212

น้ำนมเป็นสสารเหลวที่มีความซับซ้อน ซึ่งประกอบด้วย สารประกอบประเภทโปรตีน ไขมัน และเกลือแร่ ในปริมาณสูง บทบาทที่สำคัญของน้ำนม ได้แก่ การเป็นแหล่งสารอาหารที่สำคัญต่อการเจริญเติบโต เช่น เป็นแหล่งของกรดอะมิโนที่จำเป็นต่อการเจริญเติบโตของตัวอ่อน และเนื่องจากเคซีนไมเซลล์ในน้ำนมมีความสำคัญต่อคุณสมบัติของน้ำนมและผลิตภัณฑ์ การศึกษาเกี่ยวกับธรรมชาติและโครงสร้างของเคซีนไมเซลล์จึงเกิดขึ้นอย่างกว้างขวาง แต่เนื่องจากโครงสร้างที่แน่นอนของเคซีนไมเซลล์ยังเป็นข้อโต้เถียงที่หาบทสรุปแน่นอนไม่ได้ รูปแบบต่าง ๆ ของโครงสร้างของเคซีนไมเซลล์จึงถูกนำเสนอขึ้น โดยสามารถแบ่งออกได้เป็นสามกลุ่มหลัก ได้แก่ รูปแบบโค้ตคอร์ (coat-core) นำเสนอโดย Waugh และ Nobel ในปี ค.ศ. 1965, Payens ในปี ค.ศ. 1966, Parry และ Carroll ในปี ค.ศ. 1969, และ Paquin และผู้ร่วมงานในปี ค.ศ. 1987 รูปแบบนี้อธิบายถึงการเกาะกลุ่มกันของเคซีนที่มีองค์ประกอบของโครงสร้างชั้นนอกแตกต่างจากโครงสร้างชั้นใน โดยโครงสร้างชั้นในนั้นไม่สามารถระบุส่วนประกอบที่แน่นอนได้, รูปแบบซับยูนิต หรือซับไมเซลล์ (subunit หรือ sub-micelles) นำเสนอโดย Morr ในปี ค.ศ. 1967, Slattery และ Evard ในปี ค.ศ. 1973, Schmidt ในปี ค.ศ. 1980, Walstra ในปี ค.ศ. 1984, และ Ono และ Obata ในปี ค.ศ. 1989 โดยรูปแบบนี้ให้ข้อสรุปว่าเคซีนไมเซลล์ประกอบด้วยหน่วยย่อยทรงกลมหลายหน่วยที่มีองค์ประกอบคล้ายคลึงกัน และรูปแบบสุดท้าย ได้แก่ รูปแบบอินเทอร์นอล (internal) นำเสนอโดย Rose ในปี ค.ศ. 1969, Garnier และ Ribadeau-Dumas ในปี ค.ศ. 1970, Holt ในปี ค.ศ. 1992, และ Horne ในปี ค.ศ. 1998 ซึ่งรูปแบบนี้แสดงถึงวิธีการเกาะกลุ่มกันของเคซีนที่แตกต่างกัน

โปรแกรมวิชาวิทยาศาสตร์และเทคโนโลยีการอาหาร คณะวิทยาศาสตร์และเทคโนโลยี มหาวิทยาลัยราชภัฏสุรินทร์ อำเภอเมือง จังหวัดสุรินทร์ 32000

Normal bovine milk contains roughly 3.5% protein. The natural functions of milk proteins is to supply young mammals with the essential amino acids required for the development of muscular and other protein-containing tissues (Fox and McSweeney, 1998). To perfectly serve this function the milk proteins are designed in such a way that they form complexes with a comparatively large amount of calcium phosphate, which immediately coagulate in the stomach of the newborn. The major part of the milk proteins, together with calcium phosphate, occurs in the form of large colloidal particles, the casein micelles (Rollema, 1992).

The properties of many dairy products mainly depend on the properties of milk proteins, although the fat, lactose and especially the salts, are also very important. In addition, casein products are almost entirely milk protein while the production of most cheese varieties is initiated through the specific alteration of proteins by proteolytic enzymes or isoelectric precipitation. The high heat treatments to which many milk products are subjected are possible only because of the extraordinarily high heat stability of the principal milk proteins, the caseins (Fox and McSweeney, 1998). Because of their importance for the functional behavior of dairy products, caseins and casein micelles have been studied for a long time. The casein micelle occupies a unique position among biological systems because of the various different models that have been proposed for its structure. This situation has probably developed due to the complication and the relatively large size of the casein micelles, which prohibit a direct and explicit determination of the structure. Moreover, the majority of the models were based on experimental data covering a limited range of micellar properties (Rollema, 1992).

Over several decades, a variety of models have been proposed to depict the structure of bovine casein micelles. These models have generally fallen into three categories: coat-core models, subunit models, and internal structure models. Each of these categories was first proposed in the 1960s, and the original models were either abandoned or modified as supplementary information about casein micelles was obtained by subsequent researchers. The first coat-core model was proposed by Waugh and Noble in 1965, the first subunit model was proposed by Morr in 1967 the first internal structure model was proposed by Rose in 1969. More recent versions of these models were proposed for a coat-core model by Paquin and coworkers in 1987, for subunit model by Walstra in 1990, and for two new internal structure models, in which the caseins act as an inhibitor of the growth of calcium phosphate precipitates by Holt in 1992 and later in 1996 (Rollema, 1992; McMahon and McManus, 1998), and the second new model proposed by Horne in 1998 where the state of association of casein proteins is governed by a balance of attractive hydrophobic interactions and electrostatic repulsion (Horne, 1998). The objective of this article is to give an overall review of proposed models of casein micelle structure, including those in coat-core models, subunit models, and internal structure models.

1. Milk proteins

Approximately 3.0-3.5% of normal bovine milk is made up of protein; the concentration and composition of which can change during lactation. The function of milk is to supply essential amino acids that are required for the development of muscular and other protein-containing tissues in young mammals, and also for biological by active proteins providing immunoglobulins, vitamin-binding and metal-binding proteins, and several protein hormones (Fox and McSweeney, 1998). In addition, milk proteins also play a very important role in dairy and food products, e.g. during processing, including undesirable behavior such as fouling on heated surfaces, and gelling inside processing equipment (Sawyer *et al*., 2002).

Originally, milk proteins were believed to be a simple homogeneous protein, but about a century or more ago, milk proteins were divided into two broad classes (Fox and McSweeney, 1998). The first fraction, which is about 80% of the protein in bovine milk, is precipitated at pH 4.6 (isoelectric pH) at 30ºC, and is now called casein. The second minor fraction, makes up about 20% of protein, is soluble under those conditions, and is now referred to as whey protein or serum protein or non-casein nitrogen (Dalgleish, 1982; Fox and McSweeney, 1998). The rest are trace fractions of glycoproteins (Walstra *et al*., 1999).

1.1 Casein

The unique characteristic of caseins is their post-translational modifications, resulting in the phosphorylation at seryl and infrequently threonyl residues (Swaisgood, 1992). Hence, caseins are phosphoproteins containing approximately 80% of the total protein content of milk proteins (Brunner, 1977). Casein is made up of many components, and the main types are α_{s1}-casein, α_{s2}-casein, β-casein, and κ-casein (Walstra *et al*., 1999) as defined and validated by analysis of DNA sequences. There are trace amounts of γ-casein occurring naturally on account of limited proteolysis of β-casein by plasmin (Swaisgood, 1992). The main casein components have several genetic variants and contain variable numbers of phosphoseryl residues, especially α_{s2}-casein exhibiting a large variability in phosphorylation. κ-Casein contains only one phosphoseryl residue, and it is also glycosylated. Another unique feature of caseins is the large amount of propyl residues, especially in β-casein, which greatly affect the structure of caseins, because the proline residues disrupt the formation of α-helical and β-sheet (Swaisgood, 1992). In addition, all casein proteins have different hydrophobic and hydrophilic regions along the protein chain.

α_s-Caseins are the major casein proteins containing 8-10 seryl phosphate groups, while β-casein contains about 5 phosphoserine residues, and it is more hydrophobic than α_s-caseins and κ-casein. Because α_s-caseins and β-caseins are highly phosphorylated, they are very sensitive to

the concentration of calcium salts, that is, they will precipitate with excess Ca^{2+} ions. Unlike other caseins, κ-caseins are glycoproteins, and they have only one phosphoserine group. Hence, they are stable in the presence of calcium ions, and they play an important role in protecting other caseins from precipitation and make casein micelles stable (Whitney, 1988; Walstra *et al*., 1999). Casein is not heat sensitive; only temperatures up to or above 120ºC causes the casein to gradually become insoluble, whereas it is sensitive to pH and will precipitate at its isoelectric pH (Walstra *et al*., 1999).

1.2 Serum proteins

Traditionally, serum proteins or whey proteins is the term describing the milk proteins remaining in the serum after precipitation of caseins or after casein is removed (Brunner, 1977; Whitney, 1988). Whey proteins contain about 20% of the total milk protein (Fox and McSweeney, 1998). The method of casein removal from skim milk differentiates the main types of whey, acid and rennet whey, derived from the precipitation of casein with acid and by rennet enzyme, respectively (Brunner, 1977).

Most serum proteins are globular proteins with high hydrophobicity and densely folded peptide chains. They are heat-sensitive and will denature and become insoluble once milk is heated (Walstra *et al*., 1999). The two main components of serum protein in bovine milk are α-lactalbumin and β-lactoglobulin, and the rest are (blood) serum albumin, immunoglobulins, protease-peptones, and trace amount of enzymes and proteins with specific metabolic functions, such as lysozyme and lactoferrin (Brunner, 1977, Walstra *et al*., 1999).

2. Models for the structure of Casein micelles

It is now widely known that the most important biological function of milk is to supply nutrients for the offspring. To properly serve this function, milk proteins are designed to form complexes with large amounts of calcium phosphate, which immediately coagulate in the stomach of the newborn. The major part of milk proteins along with calcium phosphate occur in the form of large colloidal particles, known as casein micelles (Rollema, 1992).

About 80-95% of the casein in normal milk is in the form of colloidally dispersed particles, known as micelles (Brunner, 1977; Fox and McSweeney, 1998), containing on a dry basis of 94% protein and 6% colloidal calcium phosphate (CCP), which is comprised of calcium, magnesium, phosphate, and citrate (Fox and McSweeney, 1998). The shape of casein micelles as observed by electron microscopy is spherical, ranging in size from 50-500 nm in diameter (average about 120 nm) and a molecular mass from 106-109 Da (Brunner, 1977; Fox and McSweeney, 1998). Casein micelles are able to scatter light; therefore, the white color in milk is mainly because of light scattering by casein micelles (Fox and McSweeney, 1998).

Due to the importance of casein and casein micelles for the functional behavior of dairy products, the nature and structure of casein micelles have been studied extensively, but the exact structure of casein micelles is still under debate. Various models for casein micelle structure have been proposed (Brunner, 1977; Brule', Lenoir, and Remeuf, 2000). Most of the proposed models fall into three general categories, which are: coat-core, subunit (sub-micelles), and internal structure models (Rollema, 1992; Fox and McSweeney, 1998; McMahon and McManus, 1998).

2.1 Coat-core models

The first model fit in this class was proposed by Waugh and Nobel in 1965. This model is based originally on their studies of the casein solubility in Ca^{2+} solutions. The model depicts the formation of low weight ratio complexes of α_{s1}- and κ-caseins with the absence of calcium. From Figure 1, the α_{s1}- or β-caseins, monomers with a charged phosphate loop (Figure 1 (A)), begin to aggregate to a limiting size (the caseinate core), while the calcium ions are added. Precipitation of the caseinate is stopped after a monolayer of the low weight α_{s1}-κ-casein complexes is formed. This coat complex has the κ-casein monomers spread out completely on the surface; thus, the

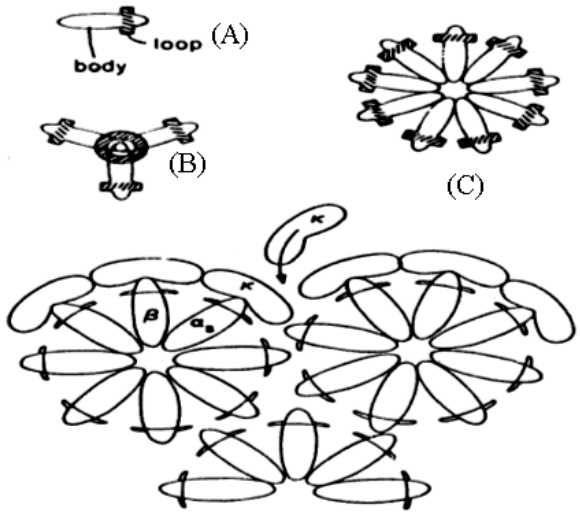


Figure 1. Waugh's proposed model for the casein micelle; (A) Monomer model for α_{s1}- or β-caseins with charged loop, (B) a tetramer of α_{s1}-casein monomers, (C) Planar model for a core polymer of α_{s1}- and β-caseins. (Source: Wong, 1988)

size of micelle is dictated by the amount of the κ-casein available. Waugh's model is able to explain the lyophilic nature of the colloidal casein complex and also the ready accessibility of the κ-casein to the enzyme chymosin (Garnier, 1973; Wong, 1988).

The second model falls in this category was proposed in 1966 by Payens based on his experimental data on the association of caseins. From Figure 2, the micelle core comprises densely folded α_{s1}-caseins molecules adhered to a loose network of β-caseins. The similar aspect of this model compared to the prior one is that the surface of the micelle is covered with κ-caseins; unlike the prior, calcium phosphate is located both on the surface and in the interior of the micelle (Rollema, 1992).

In 1969, Parry and Carroll attempted to localize κ-casein at the surface of casein micelle structure proposed by Waugh by electron microscopy using ferritin-labelled κ-casein antibodies. They found little or no concentration of κ-casein on the surface of the casein micelles. Consequently, from Figure 3, they assumed that the κ-casein might be located in the interior of the micelle and act as a point of nucleation center for α_{s1}-, β-caseins and subsequently be stabilized by CCP. The surface of this micelle model comprises α_{s1}- and β-caseins supplemented by some CCP (Wong, 1988; Rollema, 1992).

The last model to be discussed in this category was proposed by Paquin and co-coworkers in 1987. This model was based on the results obtaining from experiments completed by using monolayer methods for identifying two protein fractions from gel chromatography of EDTA-dissociated casein micelles. This model describes the micelle core as a framework of α_{s1}-caseins and CCP, where β-caseins are bound by hydrophobic interactions. The micelle core is encircled by complex particles of α_{s1}-, α-, and comparatively high proportion of κ-casein (Rollema, 1992).

2.2 Sub-micelle (subunit) models

The first sub-micelle model was proposed by Morr in 1967. This model was based on the results obtained from a study of the influence of urea and oxalate treatment on the disruption of casein micelles. Morr stated that α_{s1}-, β-, and κ-casein monomers formed small uniform sub-micelles. The sub-micelles, estimated by sedimentation velocity studies, are stabilized by hydrophobic

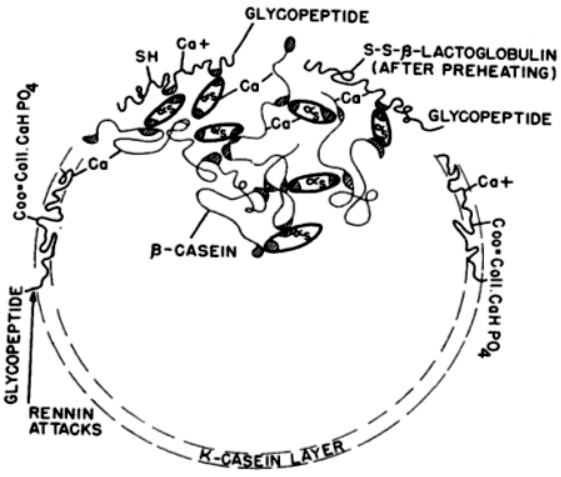


Figure 2. Coat-core model of the casein micelle proposed by Payens.
(Source: Rollema, 1992)

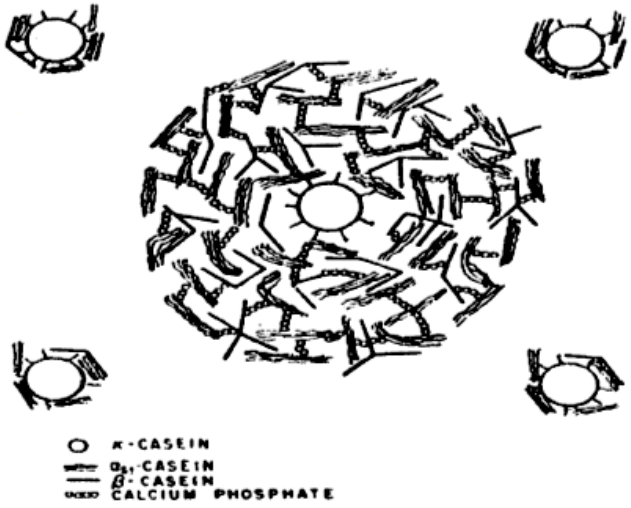


Figure 3. Casein micelle model proposed by Parry and Carroll depicting the location of κ-casein in the micelle. (Source: Wong, 1988)

bonding and calcium caseinate bridges, and the sub-micelles are aggregated and held together by CCP linkages with a micelle structure covered by α_{s1}-, and κ-casein, as seen in Figure 4 (Wong, 1988; Rollema, 1992).

The second model falls in this category was proposed by Slattery and Evard in 1973 (Figure 5). The model was based on results of experiments on the influence of calcium on the sedimentation behavior of the particles formed in mixtures of caseins. Slattery and Evard proposed that casein monomers interact with each other and form sub-micelles of variable composition with respect to their casein content. Some of the subunits in the model consists of α_{s1}-, and β-caseins, while the rest contain α_{s1}-, β-, and also κ-caseins. The κ-caseins-rich subunits are found mainly on the surface of the casein micelle, where a stabilizing force is contributed. On the contrary, subunits poor in κ-caseins will be internally buried, where hydrophobic regions are dominant. The hydrophobic regions are taken into account for the mutual

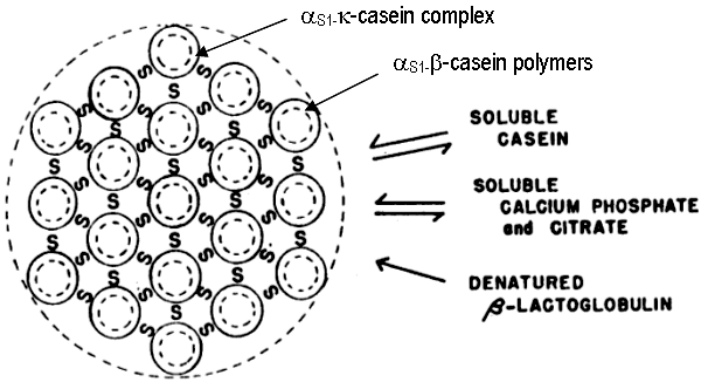


Figure 4. Casein micelle proposed by Morr with associated sub-micelles of relatively uniform composition of α_{s1}- and β-casein polymers covered with layers of α_{s1}- and β-casein complexes. S represents colloidal calcium phosphate linkages. (Adapted from: Wong, 1988)

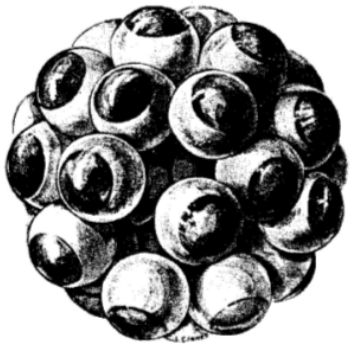


Figure 5. Casein micelle structure model from Slattery and Evard. The lighter surfaces represent α_{s1}-, and β-casein polymers (hydrophobic area). The darker patches cover about one-fifth of the surface area and represent associated κ-casein polymers (hydrophilic area). (Source: Brunner, 1977; Rollema 1992)

binding of the subunits, while the hydrophilic κ-caseins areas are exposed to the solvent at the surface. The micellar particle growth is ended when the surface of the micelle is entirely covered by the hydrophilic κ-casein regions. Hence, the size distribution of the micelles is governed by the amount if available κ-caseins (Brunner, 1977; Wong, 1988; Rollema, 1992).

In 1976, Schmidt and Payens proposed a model, which fits in this category. In this model, the subunits are presumed to be connected utterly by calcium phosphate, and they also have hydrophobic core surrounded by polar regions of element proteins. The composition of protein in sub-micelles was not identified, but κ-caseins were assumed to be localized at the surface of the micelle. Then, in 1980, Schmidt adopted Slattery and Evard's concept, where sub-micelles composed of variable protein compositions, and adapted that concept with his point of view by maintaining the idea that only calcium phosphate is responsible for the binding of the subunits, as seen in Figure 6. Subsequently, in 1982, Schmidt broadened this model with more detailed explanation of inorganic phase of the micelles (Rollema, 1992).

The most commonly accepted model in the sub-micelle model category was proposed by Walstra in 1984 (Rollema, 1992). This model suggests that casein micelles are built of roughly spherical subunits or sub-micelles. The composition of sub-micelles is variable and the size is in range 12-15 nm in diameter, and each sub-micelle has

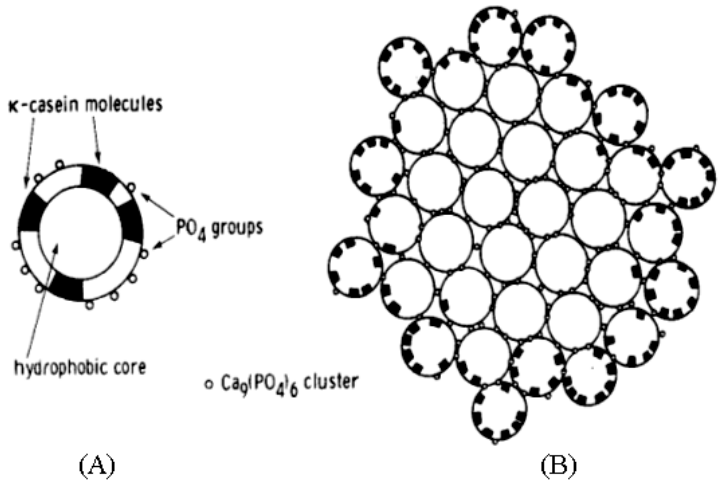


Figure 6. Casein sub-micelle model proposed by Schmidt in 1982. Schematic representation of (A) Sub-micelle, and (B) A casein micelle composed of sub-micelles. (Source: Wong, 1988; Rollema, 1992)

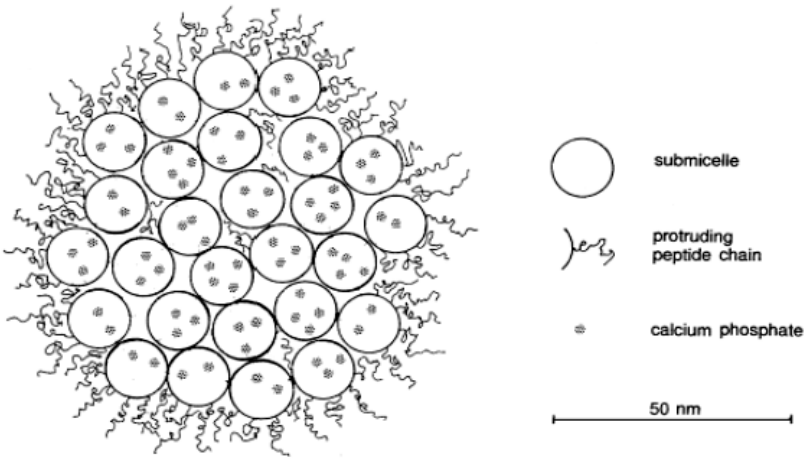


Figure 7. The structure of casein micelle in the sub-micelles model showing the protruding C-terminal parts of κ-casein as proposed by Walstra. (Source: Walstra, 1999)

20-25 casein molecules. The sub-micelles are kept together by hydrophobic interactions between proteins, and by calcium phosphate linkages. There are two main types of sub-micelles; one mainly consisting of α_s- and β-caseins, hydrophobic regions buried in the center of the sub-micelle, another type consisting of α_s- and κ-caseins, which is more hydrophilic because of the sugar residues on κ-caseins. The κ-caseins are located near the outside of the micelle with the hydrophilic part of the C-terminal end protruding from the micelle surface to form a 'hairy' layer that will avoid further aggregation of sub-micelles by steric and electrostatic repulsion. Consequently, micelles are stable, and they do not usually flocculate (Walstra, 1999; Walstra *et al*., 1999). Figure 7 shows the structure of casein micelles from the submicelles model.

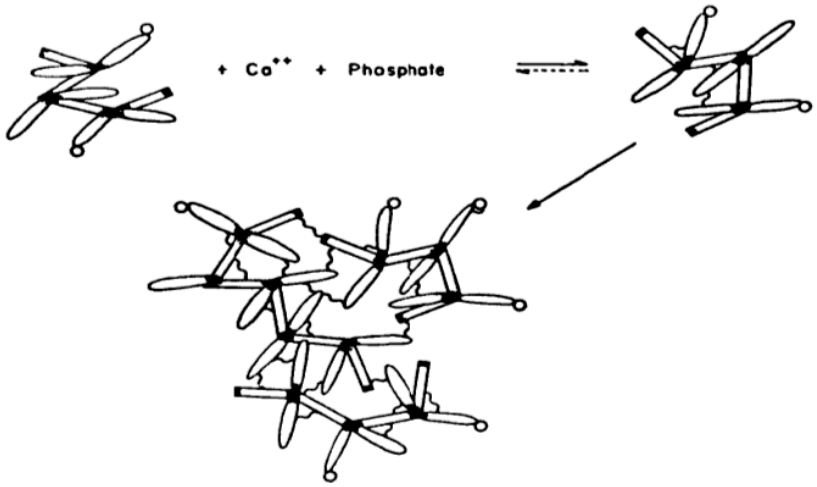


Figure 8. Schematic representation of the formation of a small casein micelle model proposed by Rose. The rods represent β-caseins, the elliptical-like rods represent α_{s1}-caseins, the circles represent κ-caseins and the S-shaped lines show chain formation. (Source: Wong, 1988)

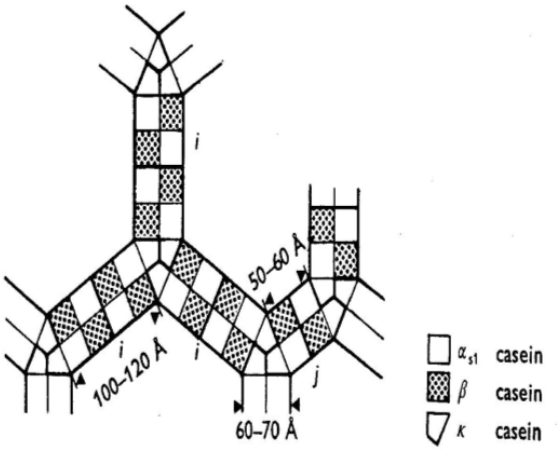


Figure 9. Part of the repeating unit of the protein network in the casein micelle in accordance with the internal structure model proposed by Garnier and Ribadeau-Dumas. (Source: Wong, 1988; Rollema, 1992)

In 1989, Ono and Obata proposed a micelle model from studies of artificial micelles prepared from protein fractions obtained by gel chromatography of calcium-depleted micelles, where the protein fractions add up to the building blocks of the micelle. In this model, micellar core comprises aggregates of α_{s1}-, and β-caseins, whereas the shell is composed of particles containing equimolar amounts of α_{s1}-, and κ-caseins. The sub-micelles are bound by colloidal calcium phosphate, and κ-casein in the shell fractions is around the surface, while α_{s1}-casein is responsible for the binding to the core sub-micelles (Rollema, 1992).

2.3 Internal structure models

The last category of models to be discussed is based on the properties of the isolated casein constituents, causing or directing the formation of the internal structure of the casein micelle (Wong, 1988).

The first internal structure model was proposed by Rose in 1969. He used the known endothermic polymerization of β-casein as the foundation for his micelle structure. Therefore, he assumed that β-casein monomers begin to self-associate into chain-like polymers. Subsequently, α_{s1}-caseins molecules are attached to the β-casein polymers, while κ-caseins interact with α_{s1}-caseins, forming aggregates of limited size. Upon forming the micelle structure, colloidal calcium phosphate acts as a stabilizing agent and cross-links the network. In addition, these micelle networks are oriented in such a way that β-casein is directed internal, while the κ-casein is directed external. However, as these threads coalesce, a small amount of κ-casein is unavoidably buried in an inward position, as seen in Figure 8 (Wong, 1988; Rollema, 1992).

Assuming a different way of association of the caseins, Garnier and Ribadeau-Dumas, in 1970, proposed a casein micelle model, which puts an emphasis on κ-casein as the keystone of micelle structure. This casein model is portrayed as a three-dimensional porous network of protein aggregates. Trimers of κ-casein act as nodes, and are linked to the three-chained-branches comprises α_{s1}-caseins and β-caseins, as seen in Figure 9. In this model, no important role of colloidal calcium phosphate was assigned, and merely a possible binding to the casein network was implied (Wong, 1988; Rollema, 1992)

Although the sub-micelle casein model as extended by Walstra (1999) has been widely accepted, two alternative models, which fall into internal structure category, have been proposed by Holt in 1992 and by Horne (1998). Holt delineated the casein micelle as a tangled web of flexible casein networks forming a gel-like structure with micro-granules of colloidal calcium phosphate through the casein phosphate center, and the C-terminal region of κ-casein extends to form a hairy layer (Figure 10). The two main features of this model are the cementing role of colloidal calcium phosphate and the surface location of hairy layer

of κ-casein. In addition, casein micelles are stabilized by two main factors, which are a surface (zeta) potential of approximately -20mV at pH 6.7, and steric stabilization owing to the protruding κ-casein layer hairs (Holt, 1994; Holt and Horne, 1996; Fox and McSweeney, 1998).

Recently, the dual bonding model of Horne (Horne, 1998), which fits into the category of internal structure models, was proposed. This model suggests that the proteins in casein micelles are bound together by two types of bonding and it is a balance between the attractive hydrophobic interactions and electrostatic repulsion. Hydrophobic interaction is the driving force for the formation of casein micelles, while electrostatic repulsions are limiting the growth of polymers or in other words defining the degree of polymerization. The conformation of α_{s1}- and β-caseins when they are adsorbed at hydrophobic interfaces form a train-loop-train and a tail-train structure, respect-

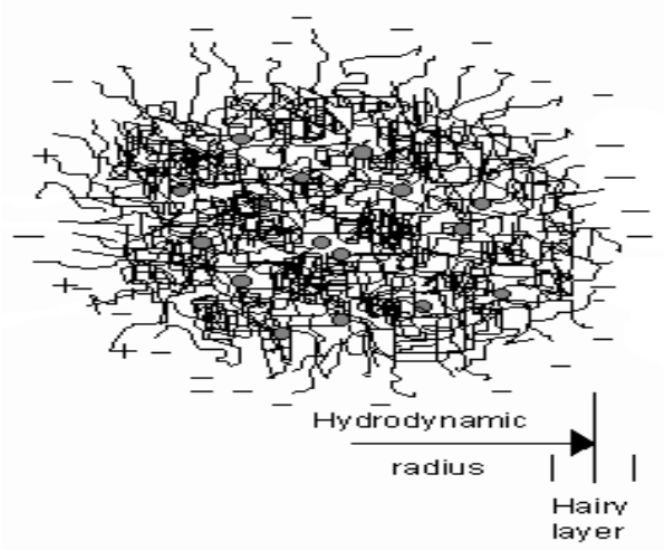
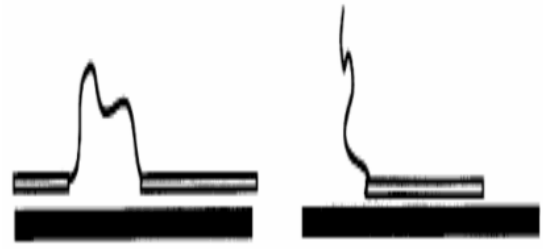
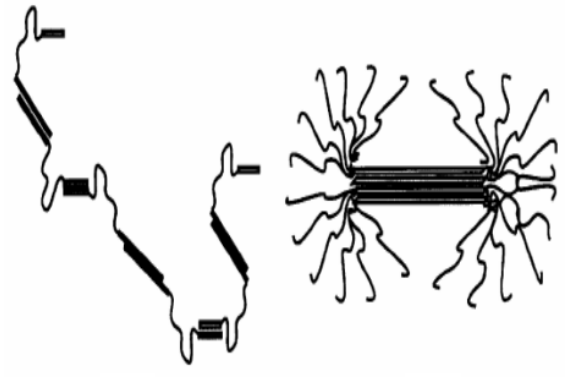


Figure 10. Hairy casein micelle model proposed by Holt, where a tangled web and open structure of polypeptide chains cross-linked by calcium phosphate nanocluster (colloidal calcium phosphate) in the core provides rise to an external region of lower segment density known as the hairy layer. The gray circles represent the calcium phosphate nanoclusters. (Adapted from: http://www.foodsci.uoguelph.ca/deicon/casein.html)



(A) **(B)**

Figure 11. Conformations of (A) α_{s1}-casein with a train-loop-train and (B) β-casein with a tail-train structure adsorbed at hydrophobic interfaces.
(Source: Horne, 1998)



(A) **(B)**

Figure 12. Polymeric structures of (A) α_{s1}-caseins and (B) β-caseins, showing linkages through hydrophobic interaction. (Source: Horne, 1998)

ively, as shown in Figure 11, and both caseins polymerize or self-associate, by hydrophobic interactions, as shown in Figure 12. Accordingly, the self-association of caseins makes it possible for polymerization to occur. Calcium phosphate nanoclusters, or CCP, are considered to be one of the linkages between casein micelles and neutralizing agents of the negative charge of the phosphoserine residues by binding to those residues; consequently, electrostatic repulsion is reduced, and the hydrophobic interaction between caseins is still dominant, resulting in more associations of proteins. Unlike other caseins, κ-caseins can only interact hydrophobically and acts as a propagation terminator, because they do not have a phosphoserine cluster to bind calcium and also another hydrophobic point to prolong to chain. The dual bonding model for the casein micelle structure is shown in Figure 13.

The α_s-, β-, and κ-caseins are shown as

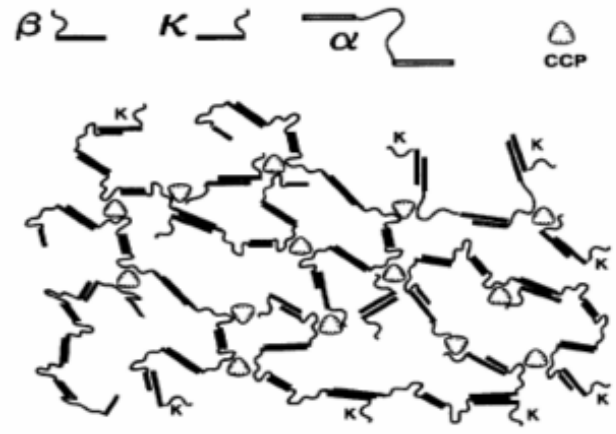


Figure 13. The dual bonding model of casein micelle structure, with α-, β-, κ-casein portrayed as indicated. Bonding appears between the hydrophobic regions, shown as rectangular bars, and by linkage of hydrophilic regions containing phosphoserine clusters to colloidal calciumphosphate clusters. Molecules of κ-casein (K) limit further growth of the structure. (Source: Horne, 1998)

indicated. Bonding between caseins first takes place in the hydrophobic regions, shown as rectangular bars, and also the linkage between CCP and phosphoserine residues of casein molecules. κ-Caseins, marked as letter K, limit further growth (Horne, 1998).

Summary

Numerous models for the structure of casein micelles have been proposed in the past three decades. Based on the chemical and physical properties of micelles, these models fit into three main categories, which are models of coat-core structure, models of sub-micelles, and models of internal structure. From the new stand point of Walstra, Holt and Horne, neither the casein micelle nor sub-micelles should be understood to be identical perfect hard spheres. The true micelles might have a structure, which is intermediate between models from Walstra, Holt, and Horne. All the models given here are helpful in explaining formation, structure, and properties of the casein micelle, and especially its reaction to changes in conditions during milk processing.

References

Brule/, G., Lenoir, J., and Remeuf, F. 2000. The casein micelle and milk coagulation. In Cheesemaking: From Science to Quality Assurance, 2nd edn. (ed. A. Eck and J. Gillis), Lavoisier Publishing, Paris, pp. 7-40.

Brunner, J.R. 1977. Milk proteins, In Food Proteins (ed. J.R. Whitaker and S.R. Tannenbaum), AVI Publishing Company, Inc., Connecticut, pp. 175-208.

Dalgleish, D.G. 1982. Milk proteins - chemistry and physics, In Food Proteins (ed. P.F. Fox and J.J. Condon), Applied Science Publishers, Ltd., Essex, pp. 155-178.

Fox, P.F. and McSweeney, P.L.H. 1998. Dairy Chemistry and Biochemistry. Blackie Academic & Professional, London.

Garnier, J. 1973. Models of casein micelle structure. Neth. Milk Dairy J., 27: 240-247

Holt, C. 1994. The biological function of casein: Research reviews, In Hannah Research Yearbook, Hannah Research Institute, Scotland, pp. 60-68.

Holt, C. and Horne, D.S. 1996. The hairy casein micelle: Evolution of the concept and its implications for dairy technology. Neth. Milk Dairy J., 50: 85-111.

Horne, D.S. 1998. Casein interactions: casting light on the black boxes, the structure in dairy products. Int. Dairy J., 8: 171-177.

McMahon, D.J., and McManus, W.R. 1998. Rethinking casein micelle structure using electron microscopy. J. Dairy Sci., 81: 2985-2993.

Rollema, H.S. 1992. Casein association and micelle formation, In Advanced Dairy Chemistry, Vol. 1: Proteins (ed. P.F. Fox), Elsevier Science Publisher, Ltd., Essex, pp. 111-140.

Sawyer, L., Barlow, P.N., Boland, M.J., Creamer, L.K., Denton, H., Edwards, P.J.B., Holt, C., Jameson, G.B., Kontopidis, G., Norris, G.E., Uhrinova, S., and Wu, S. 2002. Milk protein structure - what can it tell the dairy industry?: A Review. Int. Dairy J., 12: 299-310.

Swaisgood, H.E. 1992. Chemistry of caseins, In Advanced Dairy Chemistry, Vol. 1: Proteins (ed. P.F. Fox), Elsevier Science Publisher, Ltd., Essex, pp. 63-110.

Walstra, P. 1999. Casein sub-micelles: do they exist? Int. Dairy J., 9: 189-192.

Walstra, P., Geurts, T.J., Noomen, A., Jellema, A., and van Boekel, M.A.J.S. 1999. Dairy Technology: Principles of Milk Properties and Processes. Marcel Dekker, Inc., New York.

Whitney, R.M. 1988. Proteins of milk, In Fundamental of Dairy Chemistry, 3rd edn. (ed. N.P. Wong), Van Nostrand Reinhold, New York, pp. 81-169.

Wong, N.P. 1988. Fundamental of Dairy Chemistry, 3rd edn., Van Nostrand Reinhold, New York, pp. 481-492.