

## Partial Glycerides - An Important Nonionic Surfactant for Industrial Applications: An Overview

Kritika Sharma<sup>1</sup>, Sujata Negi<sup>1</sup>, Nandita Thakur<sup>2</sup> and Kamal Kishore<sup>1</sup>\*

<sup>1</sup>Department of Chemistry, Akal College of Basic Sciences, Eternal University, Baru Sahib 173101 (H.P.) INDIA <sup>2</sup>Department of Biotechnology, Akal College of Agriculture, Eternal University, Baru Sahib 173101 (H.P.) INDIA <sup>\*</sup>Correspondance: E-mail: <u>k\_81kishore@yahoo.co.in</u>

(Received 11 April, 2017; Accepted 30 May, 2017; Published 15 June, 2017)

ABSTRACT: Partial glycerides are esters of glycerol with fatty acids containing some unreacted hydroxyl groups. Presence of hydroxyl groups in their molecules shows that these are polar in nature. Partial glycerides may be monoglycerides (two hydroxyl groups free) or diglycerides (one hydroxyl group free). Lower carbon chain partial glycerides are more strongly polar than long chain partial glycerides. Partial glycerides contain both a lyophilic and a lyophobic group in their molecules and termed as nonionic surfactants, as they do not produce ions in solution. They are compatible with other kind of surfactants and are excellent compounds to enter complex mixtures, as found in many commercial products. Partial glycerides based surfactants are found in a large variety of domestic and industrial products. They are often found in bakery, beverages, food, pharmaceutical and cosmetic products. This review paper describes the synthesis and applications of glycerol based nonionic surfactants.

Keywords: Emulsions; Hydrophile–lipophile balance value (HLB); Antistaling agents and antistatic agents.

**INTRODUCTION:** Glycerides, more commonly known as acylglycerols, are esters formed from glycerol and fatty acids. Glycerol possess three hydroxyl functional groups, which could be esterified with one, two or three fatty acids to form monoglycerides, diglycerides, and triglycerides. Vegetable oils and animal fats contain mostly triglycerides but are broken down by natural enzymes (lipases) into partial glycerides (mono and diglycerides), free fatty acids and glycerol. Partial glycerides are nonionic type of surfactants which do not have any electrical charge. This property makes them resistant to water hardness and deactivation. They are less irritant than anionic or cationic surfactants. The hydrophobic part contains saturated fatty acid or unsaturated fatty acids or fatty alcohols. These are excellent grease/oil removers and emulsifiers. Physically partial glycerides are white or cream colored hard fats of waxy appearance, plastic products or viscous liquids. These are generally insoluble in water; soluble in ethanol, chloroform, benzene or mixtures of organic solvents. Melting point of glycerides lies in the range of 54°C to 64°C. One of the partial glycerides, glycerol monostearate ( $C_{21}H_{42}O_4$ ), commonly known as GMS, is an organic molecule (Figure 1) used as an emulsifier. GMS is a white, odorless, and sweet-tasting flaky powder that is hygroscopic. It is a glycerol ester of stearic acid.GMS is a food additive and also used as a thickening, anticaking, and preservative agent, an emulsifying agent for oils, waxes; a protective coating for hygroscopic powders; a solidifier and control release agent in pharmaceuticals. It is also used in cosmetics and hair care products. It is responsible for giving ice cream and whipped cream its smooth texture. It is sometimes used as an anti-staling agent in bread.

Monoglycerides (MG) with diglycerides, are commonly added to commercial food products in small quantities with name E471 (emulsifier), which prevent mixtures of oils and water from separating. These are often found in bakery products, beverages, ice creams, chewing gum, shortening, whipped toppings, margarine, confections, food products, pharmaceutical products and cosmetics. MG and their derivatives represent 75% of the world production of food emulsifiers (Szumała and Szeląg, 2012).

Partial glycerides occur in three major crystalline forms: alpha, beta, and beta' (beta prime). Beta forms are most stable and moderately functional, while the alpha form is the most highly functional, alphacrystalline forms can convert into the beta-crystalline forms (Figure 2). These crystalline forms are not to be confused with the description of the various molecular isomers of mono- and diglycerides determined by the position of the fatty acid on the glycerol's hydroxyl groups (Robbing and Nichoison, 1987).





Figure 1: Structure of Glycerol monostarate.

CH <sub>2</sub> COOCR	CH <sub>2</sub> OH	CH <sub>2</sub> COOCR	CH <sub>2</sub> COOCR
 снон I	 CHOOCR 	 CHOOCR	 снон I
 CH₂OH	I CH <sub>2</sub> OH	 CH₂OH	 CH <sub>2</sub> OOCR
alfa-mono	beta-mono	alfa,beta-di	alfa,alfa-di

# Figure 2: Isomers of monoglycerides and diglycerides, where –OCR represents the fatty acid moiety (Robbing and Nichoison, 1987).

**Synthesis of partial glycerides:** The monoglycerides (MG) are generally synthesized from the glycerolysis or hydrolysis of triglycerides, or the direct esterification of glycerol with fatty acids. The industrial processes involved generally use homogeneous acid or basic catalysts (Scheme 1), which lead to a mixture of mono-, di-, and triglycerides in general (40 : 50 : 10) after direct esterification (Yu et al., 2003).



#### Scheme 1: Direct esterification of glycerol with fatty acids.

Glycerol monostearate (GMS) is glycerol monoester of stearic acid (SA), having a specific hydrophilic head and a hydrophobic tail, is an important non-ionic surfactant with low hydrophile–lipophile balance value (HLB). This compound is particularly use in "water-in-oil" emulsions.GMS is conventionally prepared by the esterification of glycerol (Gly) with SA and trans-esterification of Gly with natural fats and oils, or



stearic acid methyl ester. Glycerol monostearate (GMS) which is a monoglycerides is conventionally prepared by the esterification of glycerol (Gly) with stearic acid (SA) as Scheme 2 and trans-esterification of glycerol with natural fats and oils, or stearic acid methyl ester (Han and Wang 2016).



GMS formation from GC and SA

#### Scheme 2: Esterification of glycerol (Gly) with stearic acid (SA).

Mono- and diglycerides contain a mixture of mono and diglyceryl esters of the long chain fatty acids, either saturated or unsaturated, that occurs in fats in food. The most common method for production of monoglycerides is glycerolysis, which is transesterification of triglyceride with glycerol to monoglyceride (Chetpattananondh and Tongurai, 2008).

Chemical synthesis on a large scale is based on the glycerolysis of fats and oils at high temperatures using inorganic catalysts. Pure racemic MG are prepared by esterification of 1, 2-o-isopropylidene glycerol or 1, 2-o-benzylidene glycerol with acid chlorides and the subsequent selective hydrolysis of the ketal. For the chemical synthesis of enantiomerically pure MG, sugars such as D- or L-mannitol, D- or L-arabinose, or serine derivatives have been employed as starting materials. The protected glycerol derivative 1,2-o-isopropylidene glycerol as a model substrate for transesterification and esterification reactions (Hess et al., 1994).

MG are produced by chemical synthesis in which glycerol, fat, and alkaline catalyst are mixed and heated to almost  $250^{\circ}$ C. Ca(OH)<sub>2</sub> is used as catalyst in the production of MG for the food industry. This process yields a 40–60% MG; the rest are DG and TG (Borjesson and Harrod, 1999).

The process glycerolysis has a capability of converting the free fatty acids (FFAs) to their glyceride molecules. This method involves adding glycerol to the high FFAs feedstock and heating at a high temperature about 200°C, with help of a metallic catalyst such as zinc chloride and zinc dust or without catalyst. The glycerol reacts with a free fatty acid (FFA) to form mono-glycerides, di-glycerides and tri-glycerides (Kombe et al., 2013).

Glyceryl partial esters are formed by the action of glycerol on fatty acids or natural fats to give mixtures of mono, di- and triglycerides. These mixtures may contain 40-60% of mono-esters and preparation of high proportions of mono-esters these are prepared by distillation, crystallization from solvents, chromatography, dialysis and counter-current distribution. Urea treatment of technical esters may lead to a mono- and di-glycerides, adduct formation appear to be of limited value for the fractionation of mixtures of partial esters. The two isomeric forms of the mono-esters and the isomers of the di-esters may be expected to differ in their reactions with urea, and the reactions may be modified also by the possibility that under certain circumstances alterations may occur in the equilibria between the isomeric forms of the partial esters" or between these esters and products of alcoholysis (Aylward and Wood, 1958).

Cationic exchange resins could be used in the esterification of glycerol with oleic acid in mild conditions (monoglyceride yield: 72 %), but these catalysts are less active than the homogeneous acids. In other studies it was demonstrated that the reaction between glycidol and oleic acid in the presence of anionic resins also gave a high yield of monoglycerides. However the initial preparation of the glycidol was an expensive step which decreases the interest of the process for the synthesis of the monoglycerides (Pouilloux et al., 2000).

Monoglycerides are generally obtained from the glycerolysis, hydrolysis of triglyceride (TG) and the direct esterification of glycerol with fatty acids. There are many different ways to improve the selectivity of the mono-esterification of glycerol including enzymatic methods, guanidine, solid acid catalysts (zeo-lites), and basic catalysts (ZnO). Since glycerol and fatty acids react spontaneously at 110°C and the reaction occur at high temperatures (Yu et al., 2003).

Enzymatic synthesis of MG by various lipase catalysts has received a lot of attention due to lower energy requirements and selectivity of the catalyst. Fatty acid glycerides have also been prepared by direct esterification of fatty acids or their alkyl esters with glycerol (Noureddini and Medikonduru, 1997). GMS can be synthesized enzymatically in high polar organic solvent. In these reactions water content of the reaction mixture plays an important role. Decrease in water content, decreases enzyme activity due to the insufficient hydration of the enzyme. The water content could kept constant using a pervaporation unit. A mathematical model have been estimated and experimentally verified by a set of experiments with varying and constant water contents. The highest reaction rate values were obtained for initial water content equal 0.50% (w/w). This may suggest the close to the optimal enzyme activity. Using the optimal initial water content in the reaction mixture for integrated system esterification pervaporation higher reaction rate can be expected than without pervaporation process (Ziobrowski et al., 2009).

**Applications of partial glycerides in various fields:** Glycerol derived ester based surfactants represent excellent ecological and toxicological properties. Partial glycerides is widely used in a variety of industries such as food and feed production, cosmetics pharmaceutical formulations, topical drug delivery systems, oil well drilling, textile, packaging, plastic processing and construction materials. They act as emulsifiers, emollients, lubricants and dispersants (Kandeel, 2011).

*Food industry:* Monoglycerides need to be highly pure in the food industry, because they have better emulsifying properties. To remove impurities and to increase the purity of monoglycerides up to more than 90%, vacuum or molecular distillation is conventionally applied, at laboratory scale and column chromatographic (Chetpattananondh and Tongurai, 2008).

GMS is a mixture of the monoglycerides of stearic and palmitic acid with variable quantity of di-and triglyceride these are not less than 90% total fatty acid glycerides, of which at least 35 % of monoglycerides and small quantity of stearic, palmitic and oleic acid, glycerol, water, andoleate, esters mayalsobepresent. Glycerylmonostearate is used mainly as an emollient lipophilic thickening agent. GMS commonly used in a cream formulation (Varia et al., 1987).

Partial glycerides, mono and di-glycerides constitute the major type of food emulsifiers used in many food systems and important as a basic starting material to prepare several other derivatives of modified functional properties. Each of the two processes involves several consecutive and reversible reaction steps (Zaher et al., 1998).



Phospholipids (lecithin) and MG are the most common examples of Low-molecular weight emulsifiers (LMWE) used as the stabilization of different food products, surface active compounds (emulsifiers) is required for their formation and stabilization. Phospholipids are ionizable emulsifiers which are needed to increase colloidal stability and provide interfacial interactions between food components (Pilosof et al., 2017).

Partial glycerides form normal micelles and reverse micelles structures (Figure 3) in polar and non-polar medium. Monoglycerides (MG) are the most promising polar lipid compounds able to bring new or improved functionality to food products. In food industry, monoglyceride self-assembly structures have been proposed for different applications: as structuring phase in low-fat or low saturated fat products; as systems for controlling the release of volatile aroma compounds; as a reactor for the enhancement of flavor compound formation during heat treatments (Calligaris et al., 2009).



Figure 3 Micelles formation in (a) polar medium and (b) non polar medium.

Polyglycerol esters of fatty acids, commonly used emulsifiers in food and cosmetic applications, are important to obtain information on their molecular packing at interfaces. Such information can be obtained from studies on monolayers spread at the airwater and oil-water interfaces using by surface and interfacial pressure measurement techniques (Kawaguchi et al., 2001).

Mono and diglyceride nonionic are the largest single type of food-grade emulsifiers. They are consumed used in food product. The directive of World health organization (WHO) requires that these have at least 70% mono-diglyceride, and a minimum of 30% monoacylglycerol, and that the both glycerol and triglyceride below 10% (Arcos and Otero, 1996).

The most food companies incorporate crumb softeners such as MG or diglycerides in bakery products. But the mode of action of these additives in improving the shelf life is controversial. MGs form a helical complex with the amylose fraction, thus causing a softer crumb without influencing the firming rate. Surfactants had little or no effect on initial bread crumb firmness, but they did affect the firming rate during storage (Huang and White, 1993).

MG increases the stability and improves the viscosity and life of many substances. They are biodegradable and used as food additives because of their good sensorial properties. They can be found in bakery products, instant and low-fat food, dairy products, and sauces. They also have antimicrobial activity and improve skin permeability. For these reasons, MGs are widely employed in food, cosmetics, pharmaceuticals, and plasticizer and detergent formulations. Application of enzymes as catalysts for the production of MG from oils and fats has been extensively investigated lately (Ferretti et al., 2009).

GMS is an oil-soluble surfactant with a Hydrophile -Lipophile Balance (HLB) value of 3.7. It is an important functional ingredient in a wide range of manufactured food emulsions including whippable dairy emulsions and cream liqueurs. The major functional role of GMS in ice cream is emulsion destabilization. GMS displaces protein from the fat globule surface during ageing of the ice cream mix at 57°C. This promotes emulsion destabilization and allows partial coalescence of fat droplets, which results in a product with good melt resistance and a smooth texture (Euston, 1996).

Monoglycerides of short-chain fatty acids are powerful destabilizers, whereas monoglycerides of longer chain fatty acids are not so effective. Glycerol monooleate (HLB = 2.8) is more effective destabilizer than GMS (HLB = 3.8) (Goff and Jordan, 1989).

Emulsifiers like mono and diglycerides or polyoxyethylenesorbitan esters, are used in ice creams to improve the whipping quality with smoother body and texture, and to achieve good drawing qualities at the freezer. During ice creams preparations, the whipping and concomitant freezing process imposes large shear forces on the mix. The combination of ice crystallization and shear is responsible for destabilization of the milk fat globules by an emulsifier is related to



its HLB value and the interfacial tension between the serum and lipid phases in the presence of the emulsifier (Goff et al., 1987). Saturated monoglyceride shows a lower partial coalescence rate, specifically in recombined dairy cream (Wu et al., 2016).

Fatty acid composition, glyceride form, food ingredients, pH and temperature can influence the structure behavior and stability of an emulsion. Properties such as fatty acid depend on chain length, glyceride composition and melting characteristics show a behavior of MG in emulsion systems (Timperman et al., 1996) GMS has been used as an emulsifier in food preparation and the effect of HLB of different grades of GMS of the various properties of the beads, the amount of GMS (15% w/w) and speed of agitation (1200 rpm.) was kept constant to achieve the desired quality beads by melt solidification technique (Kamble et al., 2010).

As an excipient GMS, it changes in the physicochemical, thermal, rheological, textural properties. The presence of GMS decrease the swelling power and solubility of starch, while the gelatinization temperatures and enthalpy of gelatinization increases. The change in properties of starch and noodles, with the addition of GMS found to be depending on the granule morphology. The starches with large granule populations than the potato starches with small granules and corn starch and subsequently brought greater changes in their starchand noodle properties (Kaur et al., 2005).

The ice cream containing Mono and diglycerides (MDG) and Locust bean gum (LBG) singly and combination and rang between these 0.0% to 0.14% and 0.0% to 0.23%. The ice creams containing higher concentrations of both MDG + LBG showed higher particle size values than the control, when MDG level is held constant and LBG amount increases in the ice cream. Ice creams with higher concentrations of MDG and LBG together have large difference in the rate of melting than the control. The melting rate decreases with increasing LBG concentrations at constant MDG levels. These results show that a fat aggregation may not only be affected by emulsifiers, but stabilizers may play a role in contributing to the destabilization of fat globules (Cropper et al., 2013).

Low molecular weight (LMW) emulsifiers (e.g., mono and diglycerides) and non-dairy stabilizers (e.g., alginates, carrageenans, gums and gelatins) are used in many dairy products from glycerol and fatty acids under alkaline conditions. The mono and diglycerides of fatty acids, these are common emulsifier used in ice cream. The combination of emulsifiers and stabilizers has proven to be effective in formulating functionalized liquid milk. Milk products such as yoghurts require the addition of stabilizers in order to enhance desirable characteristics such as viscosity, appearance, mouthfeel and texture. Addition of relatively low percentage of emulsifiers to low-fat ice cream provides excellent body and texture. An understanding of the interactions of these additives with the caseins, proteins, lipids and water in the native milk is important in the development of future functional and flavored dairy products (Lal et al., 2006).

The influence of GMS (saturated), glycerol monooleate (GMO unsaturated) and type of milk proteins on fat destabilization and the composition of the air interface in ice cream show that unsaturated monoacylglycerol are more powerful than saturated monoacylglycerol for displacing more proteins from the air interface. GMO strongly displaced caseins from the fat interface, introduced more partially coalesced fat adsorbed to the air interface and seemed to displace more proteins from the air interface. GMO is slightly less effective at displacing blactoglobulin from the fat interface than GMS (Zhang and Goff, 2005).

Both melting point and degradation temperature of starch are decreased by increasing glycerin content (GC). Rheologically, the addition of 2% GMS in the formulations can efficiently reduce the melt viscosity and its temperature sensitivity while imposing little effect on the non-Newtonian behavior. Moreover, the moisture sorption by the formulations could be depressed significantly by incorporating a small amount of GMS (Liu et al., 2001).

There are significant interactions between waxy corn starch and MG, as purposed by the measurement of starch MG complex formation, iodine affinitity, differential scanning calorimetry and texture measurements in model systems. All MGs form some amount of complex with waxy corn starch. The titrations of the complexes also show that the presence of MGs significantly decreased the iodine affinity of the amylopectin when compared with the control (Huang and White, 1993).

Addition of GMS to maize starches with different amylose contents can form inclusion complexes. The complexes formation between the NMS (Normal maize starch) or HAMS (High Amylose maize starch) and GMS, affect the physicochemical properties viz. decrease in leached amylose, solubility and delayed the gelatinization of these starches. The quantities of the emulsifier and amylose have direct influence on



the complex formation. GMS concentration lower than 2% is necessary to complex with available amylosein NMS, while at least 3% GMS is necessary in HAMS (Garcia and Franco, 2015).

**Drug and cosmetics:** Partial glycerides, like glycerol monooleate (GMO) and glycerol monostearate (GMS), are self-assembling amphiphilic molecules. They form a variety of crystalline structures with useful mechanical properties are of special interest in drug delivery. Monoglycerides exhibit complex solid-state behavior including melting, crystallization and physical modifications during processing and storage. The melting and crystallization pattern of a matrix of mixed monoglyceride polymorphs is known to be a function of the composition and can be systematically to achieve desirable properties (Mengesha et al., 2013).

Due to versatile structural appearance, partial glycerides offer a wide range of different possibilities for pharmaceutical formulation purposes. These substances are bio-degradable and physiologically non-toxic. Lipids can be used to enhance solubility and permeability of drugs exhibiting poor bioavailability (Windbergs et al., 2009).

Partial glycerides consisting of a mixture of glyceryl acids fatty is composed of ester of glycerylmonostearate (65%), glycerylmonopalmitate (30%) glycerylmonomyristate and (5%). The effect of different HLB of glyceryl monostearate i s significant. The beads containing low HLB GMS sh owed faster drug release than the high HLB GMS (Kamble et al., 2010).

Partial glyceride (glyceryl monostearate) is a lipophilic substance; its incorporation could render the matrix system more lipophilic. Increase in the lipophilicity can decrease the rate of water penetration cause in a slower rate of drug release. lipophilicity can be a possible mechanism for drug retardation from the glyceryl monostearate matrix system (Peh et al., 2000).

A spontaneous behavior of Stearic acid in the presence of its monoglyceride and evaluated its potential to be used as drug delivery vehicle, without using any solvent. Feasibility of drug delivery vehicle for ciprofloxacin has evaluated. The efficiency of ciprofloxacin hydrochloride (CF) is found to be 13 + 3% and 32 +4.2% when the formulation is prepared at pH 5.5 and 9.5, respectively. The size of the vesicles is found in the range of 1–3 mm. These formulations are found to be biocompatible when studied against J774 macrophages (Mishra et al., 2009).

Some partial glycerides, like unsaturated MG(glycerol monooleate or linoleate) belonging to the class of water-insoluble swelling lipids, represents an interesting class of compounds in industry. Depending on water content and temperature, such MG can form various mesophases. GMS has a low-viscosity microemulsions by addition of short-chain alcohols, alcohol decreases the polarity of water and provides an environment with a balance of lipophilic–hydrophilic properties (Antona et al., 2000).

GMS have a broad range of applications from stabilizer to release agent in industries like food and personal care, as well as general industrial applications such as adhesives and textiles (Sousa et al 2007). Glycerol monostearate matrix used as one of the basic constituent materials in cosmetic cream. Nanogold bound in this material will be used in modern material of anti-aging cosmetic along with other basic constituents (Taufikurohmah et al., 2011).

Other Industrial applications: Partial glycerides, have important industrial application other than food, drug & cosmatics industries. They are use in agriculture as antifogging agents, polymer industry as additives, textiles as lubricants, in paint industry as emulsifier etc. Glycerol monosterate and magnesium stearate have shown the most effective anti-sticking agents led to a clear decrease in tackiness of the chitosan films because low values of minimum fluidization velocity (Cervera et al., 2004). Partial glycerides e.g. GMS is a favorable fatty acid ester with the high energy storage capacity, suitable phase change temperature, good thermal reliability and chemical stability. Therefore is known as a novel solid-liquid organic phase change materials (PCM) for storage and retrieval of thermal energy (Ke et al., 2013). Some important applications of glycerol monostearate are mentioned in Table 1. These are also used as synthetic intermediates and chiral building blocks in synthetic organic chemistry (Kumoro, 2012).

### Table 1: Some potential application of glycerolmonostearate (GMS) - a partial glyceride.

S.No.	Potential applications	Reference
1	Emulsifying agents in cos- metic industry promotes the emulsification.	Yu et al., 2003



2	Preservative agent in Bread packaging.	He and Hoseney, 1990
3	Stabilizer in candy, choco- lates and magarine to flovour.	Biliaderis and Seneviratne, 1990
4	Softner improvement in crispness in biscuit dough.	Manohar and Haridas, 1999
5	Antibiotics in delivery used as a prevention of surgical wound infection.	Allababidi And Shah, 1998
6	Improve texture and reduce adhesiveness.	Wang et al., 2013
7	Antistaling agents in bakery products.	Gray et al., 2003
8	Additives in milling indus- tries to improve the function- al characteristics of wheat flour.	Ravi et al., 1999
9	Anticaking agents are added to improve the flowability and to inhibit the tendency to cake.	Jaya S and Das H, 2004
10	Antistatic agents for thermo- plastic polymers.	Marcat and Cecchin, 1996
11	Lubricants in textile industry to increase smoothness.	Castello and Mat- tocks, 1962
12	Antifog additives used in agricultural.	Irusta et al., 2009
13	Controlling food dispersions (dispersant).	Valero et al., 2017

Glycerol monostearates act as phase change materials (PCMs). Nanofibers formed depends upon glycerol monostearate/polyethylene terephthalate (GMS/PET) composite, in which GMS acted as solid-liquid PCMs and PET served as supporting skeleton. The morphological investigations revealed that the maximum mass ratio of GMS/PET in the composite phase change nanofibers could reach up to 1.5/1 wt. %, and the GMS component acting as, phase separated domains are randomly distributed and embedded inside the three-dimension network structure of the PET nanofibers without any leakage. FT-IR results confirmed that there is no chemical reaction between GMS and PET molecules. DSC analysis results suggested that the GMS/PET composite nanofibers are efficient thermal energy storage material with high energy storage capacity and appropriate transition temperature (Ke et al., 2013).

GMS and gum rosin (GR) used to increase the organo layer silicate (OLS) gallery or intercalation and temperature stability as it provides an advantage for OLS to ease the exfoliation process. It is observed that OLS, and using GMS and GR, improved the interlayer gallery, and the improvement is getting higher with the increasing of concentration. It is expected that the partial glyceride (GMS) is stable in the interlayer gallery during the biodegradable compounding (Liza et al., 2012).

The combination two surfactants with same ratio provide a synergistic behavior, the dynamic film properties and potentially show that lecithin dominated the surface of oil droplets, providing stability to the emulsions against flocculation and coalescence, while allowing the formation of small oil droplets. However, higher value of interfacial pressure is attained at initial times when lecithin and GMS are with same ratio. Interfacial visco-elasticity and viscosity of mixed films are similar to that of lecithin alone. However, emulsions viscosity is dominated by GMS. The synergistic performance of lecithin-GMS blends as stabilizers of oil in water emulsions is attributed to their interaction both in the bulk and at the interface. The stability, dynamic interfacial properties and rheology of emulsions are greatly affected by the combination of two low-molecular weight emulsifiers like lecithin and GMS (Valero et al., 2017).

Environmental pH, affects the stability of gel phase of GMS-water systems, using sodium stearoyllactylate (SSL) and sodium stearate (NaS) as co-emulsifers. NaS in MG-gels may be present in a micellar phase and lamellar phase. Above the critical micellar concentration of NaS, the NaS solution and diluted MG-gels remained at a stable pH (Figure 4). MG-gels prepared using NaS formed a more stable a-gel phase, but the co-emulsifiers possibly arranged in micelles and incorporated into the lamellar structure of GMS at the same time. In practice, environmental pH should be taken into consideration together with the type and concentration of co-emulsifiers used in MG structured systems (Wang and Marangoni, 2015).



Figure 4: The pH of MG-gels and NaS dilute solutions, and cmc value of NaS shown by vertical dotted line (Wang and Marangoni 2015).



**CONCLUSION:** Partial glycerides contain both a lyophilic and a lyophobic group in their molecules and termed as nonionic surfactants, as they do not produce ions in solution. Due to nonionic character these are compatible with other kind of compounds and are excellent candidate to enter complex mixtures, as found in many commercial products. These are generally synthesized from the glycerolysis or hydrolysis of triglycerides, or the direct esterification of glycerol with fatty acids. Partial glycerides is widely used in a variety of industries such as food and feed production, cosmetics, pharmaceutical formulations, topical drug delivery systems, oil well drilling, textile, packaging, polymers processing, construction materials and nanotechnoloy etc.

**ACKNOWLEDGEMENT:** The authors are grateful to Hon'ble Vice Chancellor, Prof. H.S. Dhaliwal and Dean (PG) Prof. B.S. Sohal, Eternal University, Baru Sahib (Himachal Pradesh) India for their constant encouragement and logistic supports.

#### **REFERENCES:**

- 1. Szumała P. and Szeląg H. (2012) Water Solubilization Using Nonionic Surfactants from Renewable Sources in Microemulsion System. J. Surfactant and Detergents 15(4): 485–494.
- 2. Robbing S. J. and Nichoison S. H. (1987) Long term stability studies on stored glycerolmonostearate (GMS) effect of relative humidity. *JAOCS* 64(1): 120-124.
- **3.** Yu C., Lee Y., Cheon B., and Lee S. (2003) Synthesis of Glycerol Monostearate with High Purity. *Bull. Korean Chem. Soc.* 24(8): 1229-1231.
- **4.** Han L. and Wang T. (2016) Preparation of glycerol monostearate from glycerol carbonateand stearic acid. *RSC Advance* 6: 34137–34145.
- Chetpattananondh P. and Tongurai C. (2008) Synthesis of high purity monoglycerides from crude glycerol and palm stearin. J. Sci. Technol. 30(4): 515-521.
- Hess R., Bornscheuer U., Capewell A. and Scheper T. (1994) Lipase-catalyzed synthesis of monostearoylglycerol in organic solvents from 1,2–O- sopropylidene glycerol. *Enzyme Microb.Technol* 17: 725-728.
- Borjesson I. and Harrod M. (1999) Synthesis of Monoglycerides by Glycerolysis of Rapeseed Oil Using Immobilized Lipase. JAOCS 76(6): 701– 707.
- 8. Kombe G. G., Temu A. K., Rajabu H. M., Mrema G. D. and Lee K. T. (2013) Low

Temperature Glycerolysis as a High FFA Pre-Treatment Method for Biodiesel Production. *ACES* 3: 248-254.

- **9.** Aylward F. and Wood P. D. S. (1958) Studies On Glyceryl Esters The Use Of Urea Inclusion Compounds For The Fractionation Of Technical Monoglycerides. *J. appl. Chem.* 7: 561 -565.
- PouillouxY., Tayer S. B. M. and Barrault J. I. (2000) Synthesis of glycerol monooctadecanoate from octadecanoic acid and glycerol. Influence of solvent on the catalytic properties of basic oxides. *C. R. Acad. Sci. Paris: Chemistry* 3: 589–594.
- **11.** Noureddini H. and Medikonduru V. (1997) Glycerolysis of Fats and Methyl Esters. *JAOCS* 74(4): 419-425.
- **12.** Ziobrowski Z., Kiss K., Rotkegel A., Nemestothy N., Krupiczka R. and Gubicza L. (2009) Pervaporation aided enzymatic production of glycerol monostearate in organic solvents *Desalination* 241: 212-217.
- **13.** Kandeel E M (2011) Synthesis and Performance of Glycerol Ester-Based Nonionic Surfactants. *Pelagia Research Library* 2(3): 88-98.
- 14. Varia S., Laughlin R., Sachs C., Brittain H., Cohen E. and Timmins P. (1987) Effects of variations in physicochemical properties of glycerylmonostearate on the stability of an oil-in water cream. J. Soc. Cosmet. Chem. 40: 215-229.
- **15.** Pilosof M. R., Moria M. I. and Henestrosa V. M. (2017) Synergistic performance of lecithin and glycerol monostearate in oil/water emulsion colloids and surface B. *Biointerfaces*151: 68-75.
- Calligaris S., Pieve S. D., Arrighetti G and Barba L. (2010) Effect of the structure of monoglyceride-oil-water gels on aroma partition. Food Research International 43(3): 671–677.
- **17.** Arcos J. A. and Otero O. (1996) Enzyme, medium and reaction engineering to design a low-cost, selective production method for mono and dioleoylglcerol. *JAOCS* 76(6): 673-682.
- **18.** Huang J. J. and White P. J. (1993) Waxy Corn Starch: Monoglyceride Interaction in a Model System. *AACC* 70(1): 42-47.
- **19.** Ferretti C. A., Olcese R. N., Apesteguia C. R. and Cosimo J I D (2009) Heterogeneously-Catalyzed Glycerolysis of Fatty Acid Methyl Esters: Reaction Parameter Optimization. *Ind. Eng. Chem. Res.* 48 (23): 10387–1039.
- **20.** Euston S. E., Singh H., Munro P. A. and Dalgleish D G (1996) Oil-in-Water Emulsions Stabilized by Sodium Caseinate or Whey Protein Isolate as influenced by Glycerol Monostearate. *Journal of Food Science* 61(5): 916-920.



- **21.** Goff H. D. and Jordan W. K. (1989) Action of Emulsifers in Promoting Fat Destabilization During the Manufacture of Ice Cream. *Journal of Dairy Science* 71(1): 18-29.
- **22.** Goff H. D., Uboff M., Jordan W. K. and Kinsella J. E. (1987) The effects of polysorbate 80 on the fat emulsion in ice cream mix evidence from transmission electron microscopy studies. *Food microstructure*6: 193-198.
- **23.** Wu S., Wang G. Lu Z., Li Y., Zhou X., Chen L., Jialu C. J. and Zhang L. (2016) Effects of glycerol monostearate and Tween 80 on the physical properties and stability of recombined low-fat dairy cream. *Dairy Sci. & Technol.* 96 (3) 377–390.
- 24. Timperman K. C., Choi J. H., and Flores R. J. (1996) Mono- and Diglycerides Prepared by Chemical Glycerolysis from a Butterfat Fraction. *Journal Of Food Science* 61(1): 44-47.
- **25.** Kamble R., Kumar A., Mahadik K. and Paradkar A. (2010) Ibuprofen-glycerylmonostearate (Gms) beads using melt solidification technique: Effect of HLB. *Int J Pharm PharmSci.* 2(4): 100-104.
- **26.** Cropper S. L., Vurma N. A. K., Tharp B. W. and Harper W. J. (2013) Effects of Locust Bean Gum and Mono - and Diglyceride Concentrations on Particle Size and Melting Rates of Ice Cream. *Journal of Food Science* 78(6): 811-816.
- 27. Lal S. N. D., Connor C. J. and Eyres L. (2006) Application of emulsifiers/stabilizers in dairy products of high rheology. *Advances in Colloid and Interface Science*123–126: 433–437.
- **28.** Mengesha A. E., Wydra R. J., Hilt J. Z. and Bummer P. M. (2013) Binary Blend of GlycerylMonooleate and GlycerylMonostearate for Magnetically Induced Thermo-Responsive Local Drug Delivery System. *Pharm Res*30: 3214–3224.
- **29.** Peh K. K., Wong C. F. and Yuen K. H. (2000) Possible Mechanism for Drug Retardation from GlycerylMonostearate Matrix System. *Drug Development and Industrial Pharmacy* 26(4): 447–450.
- **30.** Mishra P R, Gupta G K, and Jain V (2009) Stearic Acid and GlycerylMonostearate Based Self-Assembled Vesicles: Preparation and In vitro Evaluation. *Journal of Dispersion Science and Technology* 30: 1449–1457.
- **31.** Antona P. D., Parker W. O., Zanirato M. C., Esposito E. and Nastruzzi C. (2000) Rheological and NMR characterization of monoglyceride based formulations. John Wiley & Sons 13: 40-52.

- 32. Sousa A. R., Simplicio A. L., Sousa H. C. D. and Duarte C. M. M. (2007) Preparation of glycerylmonostearate-based particles by PGSS®—Application to caffeine. J. of Supercritical Fluids43: 120–125.
- **33.** Taufikurohmah T., Sanjaya1 I. G. M. and Syahrani A. (2011) Nanogold Synthesis Using Matrix Mono Glyceryl Stearate as Antiaging Compounds in Modern Cosmetics. *Journal of Materials Science and Engineering A 1*: 857-864.
- **34.** Laughlin R., Sachs C., Brittain H., Cohen E., Timmins P., and Varia S. (1987) Effects ofvariations in physicochemical properties of glycerylmonostearate on the stabilityof an oilinwater cream. *j. Soc.Cosmet. Chem.* 40: 215-229.
- **35.** Cervera M. F., Heinamaki J., Rasanen E., Antikainen O., Nieto O. M., Colarte A. I. and Yliruusi J. (2004) Determination of tackiness of chitosan film-coated pellets exploiting minimum fluidization velocity. *International Journal of Pharmaceutics*281:119–127.
- **36.** Ke H., Li D., Wang X., Wang H., Cai Y., Xu Y., Huang F. and Wei Q. (2013) Thermal and mechanical properties of nanofibers-based formstable PCMs consisting of glycerol monostearate and polyethylene terephthalate. *J Therm Anal Calorim* 114(1): 101-111.
- **37.** Kumoro A. C. (2012) Modeling Studies of the Reaction Kinetics of Alkaline-Catalyzed used Frying Oil Glycerolysis using Isopropyl Alcohol as a Reaction Solvent. *Research Journal of Applied Sciences, Engineering and Technology* 4(8): 869-876.
- **38.** Garcia M. and Franco C. (2015) Effect of glycerol monostearate on the gelatinization behavior of maize starches with different amylose contents. *Starch/Starke*67: 107–116.
- **39.** Liu Z. Q., Yi X. S. and Feng Y. (2001) Effects of glycerin and glycerol monostearate on performance of thermoplastic starch. *Journal of material science*.36: 1809–1815.
- **40.** Liza C., Soegijono B., Budianto E., Alinasiri J. and Jayatin (2012) Effect of Pretreatment of Organo Layer Silicate with Surfactant Using Sonication to the Gallery of Silicate Layer for Biodegradable Nanocomposite Preparation. *Procedia Chemistry*4: 47–52.
- **41.** Valero M. I. M., Henestrosa V. M. P. and Pilosof A. M. R. (2017) Synergistic performance of lecithin and glycerol monostearate in oil/water emulsions Colloids and Surfaces B: *Biointerfaces*151: 68–75.



- **42.** Zhang Z. and Goff H. D. (2005) On fat destabilization and composition of the air interface in ice cream containing saturated and unsaturated monoglyceride. *International Dairy Journal* 15: 495–500.
- **43.** Wang F. C. and Marangoni A. G. (2015) pH and stability of the a-gel phase in glycerolmonostearate–water systems using sodium stearoyllactylate and sodium stearate as the coemulsifier. *RSC Adv*. 5: 96746–96749.
- **44.** Windbergs M., Strachan C. J. and Kleinebudde P. (2009) Influence of the composition of glycerides on the solid-state behavior and the dissolution profiles of solid lipid extrudates. *Int. J. Pharm.*318: 184–191.
- **45.** He H. and Hoseney R. C. (1990) Changes in Bread Firmness and Moisture During Long-Term Storage. *Cereal Chem.* 67(6): 603-605.
- **46.** Biliaderis C. G. and Seneviratne H. D. (1990) Solute effects on the thermal stability of glycerol monostearate-amylose complex superstructures. *Carbohydrate Research*208: 199-213.
- **47.** Manohar R. S. and Haridas Rao P. H. (1999) Effect of emulsifiers, fat level and type on the rheological characteristics of biscuit dough and quality of biscuits. *J Sci Food Agric*79: 1223– 1231
- **48.** Allababidi S. and Shah J. C. (1998) Kinetics and Mechanism of Release from Glyceryl Monostearate-Based Implants: Evaluation of Release in a Gel Simulating in Vivo Implantation. *Journal of Pharmaceutical Sciences* 8(6): 738-744.
- **49.** Wang J. P., An H. Z., Jin Z. Y., Xie Z. J., Zhuang H. N. and Kim J. M. (2013) Emulsifiers and thickeners on extrusion-cooked instant rice product. *J Food SciTechnol* 50(4): 655–666.
- **50.** Gray J. and Bemiller J. (2003) Bread Staling: Molecular Basis and Control. *Comprehensive Review In. Food Science and Food safety* 2: 1-21.
- **51.** Ravi R., Manohar R. S. and Rao P. H. (1999) Use of Rapid Visco Analyser (RVA) for measuring the pasting characteristics of wheat flour as influenced by additives. *J Sci Food Agric*79: 1571–1576.
- **52.** Marcat B. and Cecchin G. (1996) Analysis of mixtures containing free fatty acids and mono-, di and triglycerides by high- performance liquid chromatography coupled with evaporative light-scattering detection. *Journal of chromatography*73: 83-90.
- **53.** Castello R. A. and Mattocks A. M. (1962) Discoloration of Tablets Containing Amines and

Lactose. *Journal of Pharmaceutical Sciences* 51(2): 106-108.

- **54.** Irusta L., Gonza A., Berridi M. J. F., Iruin J. J., Asu J. M., AlbizuI, Ibarzabal A., 1. A. Salmero A., Fontecha A., Garcı Y. and Real A. I. (2009) Migration of Antifog Additives in Agricultural Films of Low-Density Polyethylene and Ethylene-Vinyl Acetate Copolymers Journal of Applied Polymer Science 2299- 2307.
- **55.** Kaur L., Singh J. and Singh N. (2005) Effect of glycerol monostearate on the physico-chemical,thermal, rheological and noodle making properties of corn and potato starches. *Food Hydrocolloids*19: 839–849.
- **56.** Kawaguchi M., Midori Yamamoto M., Nakamura T., Yamashita M., Kato T. and Kato T. (2001) Surface Properties of Mono-, Di-, and Triglycerol Monostearate Monolayers Spread at the Air-Water Interface. *Langmuir.* 17: 4677-4680.
- **57.** Zaher F. A., Aly S. and El-Kinawy O. S. 1998) Lipase - Catalyzed glycerolysis of sunflower oil to produce partial glycerides. *Grasas y Aceites*. 49 (5-6): 411-414.
- **58.** Jaya S. and Das H. (2004) Effect of maltodextrin, glycerol monostearate and tricalcium phosphate on vacuum dried mango powder properties. *Journal of Food Engineering* 63: 125–134.

