Lipase Catalysis in Presence of Nonionic Surfactants

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Abstract

Lipase can catalyze varieties of reactions at the interface of aqueous and organic phase. Among various alternatives to modify catalytic performance of lipase, the addition of surfactants, particularly nonionic surfactants, has been widely studied. Low concentrations of nonionic surfactants augment lipase catalysis; on increasing surfactant concentration, often the catalytic performance decreases. Mole ratio of water to (nonionic) surfactant also has a profound effect on lipase activity. Catalytic abilities of some lipases are either enhanced or reduced in the presence of all nonionic surfactants of the same type, whereas for some other lipases, nonionic surfactants of the same type have mixed effect. Nonionic surfactant even changes substrate specificity of lipase. Water-in-ionic liquid microemulsion involving nonionic surfactant often performs better than other systems in improving catalytic ability of lipase. Tween and Triton surfactants often enhance enantiomeric separation catalyzed by lipase. Nonionic surfactants significantly affect activities of immobilized lipase, being present either as a component during immobilization or as a component in reaction medium. Lipases coated with nonionic surfactants act better than reverse micelles and microemulsions containing lipase. Thus, nonionic surfactants help lipase catalyzed processes in various media to enhance production of useful compounds like flavor ester, structured lipids, optically pure compounds, and noncrystalline polymers.

Keywords Biocatalysis · Enzymatic reactions · Immobilization · Lipase–additive interaction · Surfactant-coated lipase

Introduction

Lipase, an enzyme of the class *hydrolase*, requires biphasic media comprising of a polar medium (to solubilize lipase) and a nonpolar medium (to solubilize substrates) in order to

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manifest catalytic action. Nonpolar medium like organic solvent inactivates lipase, either partially or completely. Hydrated surfactant aggregates like micelles, reverse micelle (RM), and microemulsions can solve this problem by increasing substrate solubilization and guarding lipase from a denaturing effect of organic solvent [1]. Factors like micelle formation, concentrations of free and micellar substrate, and their availability to lipase make molecular interactions complex. Conformational change of lipase from closed to open form leads to access of active site by substrate. As a large hydrophobic surface is exposed around active site in open conformation, only closed form is observed in water [2]. Surfactants preferentially interact with some of the binding sites of enzyme or form more powerful hydrophobic bonds than existing ones and thus change its structure and, simultaneously, catalytic ability [3]. High activity of lipase can also be achieved through stabilization of the hydrophobic surface by substrate or premicellar surfactant assemblies [4]. Surfactants can affect the interaction between protein (enzyme) and lipidic interface also [5].

As lipase acts at a hydrophobic/hydrophilic interface, catalytic activity of a specific lipase in micelle varies with a hydrophilic head group of respective surfactant [5]. Cationic and anionic surfactants have cationic and anionic head groups, respectively, which have denaturing effects on lipase due to electrostatic interactions. Nonionic surfactants with uncharged polar head groups cannot have any electrostatic interaction with enzyme. Naturally, these surfactants cannot deactivate enzyme like lipase through conformational changes, rather stabilize it through hydrogen bonding and hydrophobic interactions and work as a lipase activator through an increasing lipid–water interfacial area [6, 7]. Surfactant-induced structural change like helicity played a significant role in controlling the catalytic performance of lipase [8]. Nonionic surfactants, with 100 times smaller critical micellar concentration (CMC) than ionic surfactants containing similar hydrophilic groups, can solubilize more substrates by forming more micelles and thus can augment catalysis [3].

But, nonionic surfactants can inactivate enzymes at high concentrations (equal to or more than CMC) [9]. At extremely high concentrations of surfactant (a few times of CMC), most of the free substrate, being incorporated into micellar phase, was unavailable to lipase, leading to low lipase activity [10]. Nonionic surfactant types like Span (ester of sorbitol with fatty acid), Tween (contains additional polyethylene glycol segment over *Span* structure), and Triton (constitutes of octylphenoxy and ethoxy groups) have differences in their structure. Water-insoluble Span surfactants act as water-in-oil emulsifiers, but water-soluble Tween and Triton surfactants act as oil-in-water emulsifiers. Consequently, these surfactants affect the catalytic ability of lipase differently. The present work discusses impacts of various nonionic surfactants on catalytic abilities of lipases from different origins.

Effects of Nonionic Surfactants on Catalytic Ability of Free Lipase

Span, Tween, and Triton surfactants have widely varying effects on catalytic performances of different (free) lipases. Table 1 shows that sorbitan monooleate (Span 80) enhanced the catalytic activity of *Candida rugosa* lipase (CRL) but decreased the activity of porcine pancreas lipase (PPL) [11, 12]. Table 2 represents impacts of Tween surfactants on the catalytic performance of various free lipases [9, 10, 12–20]. Polyethylene glycol sorbitan monooleate (Tween 80) enhanced catalytic activities and enantioselectivities of some lipases [14–16] but reduced activities of some other lipases [12, 17–19]. Table 3 shows

Table 1 Effects of Span surfactants on catalytic abilities of free lipases

Surfactant concentration	Source/type of lipase	Details of reaction	Effects on catalytic abilities of free lipases	Reference
Span 80				
0.02 M	CRL	Castor oil hydrolysis	38% enhancement in ricinoleic acid production	[11]
0.01 M	PPL	Mustard oil hydrolysis	75% decrease in erucic acid production at 1 g buffer/g oil	[12]
Span 65				
0.005 M	*Candida antarctica* lipase (CAL)	Structured phenolic lipid synthesis from flaxseed oil transesterification with phenolic acid in a solvent-free system	Enhancement in total phenolic lipid yield from 62.6 to 66.5%	[13]

that Triton surfactants augmented activities of some lipases [9, 10, 15, 18, 21, 22] but reduced activities of some other lipases [12, 17, 23]. The results from Tables 1, 2, and 3

Table 2 Effects of Tween surfactants on catalytic abilities of free lipases

Surfactant concentration	Source/type of lipase	Details of reaction	Effects on catalytic abilities of free lipases	Reference
Tween 80				
0.01 M	PPL	Mustard oil hydrolysis	84% decrease in erucic acid production at 1 g buffer/g oil	[12]
	Pseudomonas aeruginosa BN-1		1.2 times activity increase	[14]
CMC	*Rhizopus homothallicus*		25% activity increase	[15]
2%, *w/v* (∼0.015 M)	CRL	2-Chloroethyl ketoprofenate hydrolysis	Improved enantioselectivity	[16]
	Bacillus cereus C$_7$	Olive oil hydrolysis	5% activity decrease	[17]
	Fusarium oxysporum		30% activity decrease	[18]
	Oilseeds of *Pachira aquatica*	*p*-Nitrophenyl acetate hydrolysis	at < 0.002 M, Tween 80 inhibited more than Triton X-100; at > 0.002 M, it is reversed	[19]
Tween 20				
Below CMC	*Bacillus cereus* C$_7$	Olive oil hydrolysis	5% activity decrease	[17]
	Thermosyntropha lipolytica		Moderate activation	[20]
0.25% (∼0.002 M)	CVL		Highest activity	[9]
0.03% (∼0.00024 M)	*Bacillus* sp.		Highest activity	[9]
0.000049 M	Kid pregastric lipase	*p*-Nitrophenyl butyrate hydrolysis	35% activity increase	[10]
Tween 40				
	Fusarium oxysporum		20% activity decrease	[18]

Table 3 Effects of Triton surfactants on catalytic abilities of free lipases

Surfactant concentration	Source/type of lipase	Details of reaction	Effects on catalytic abilities of free lipases	Reference
Triton X-100				
0.01 M	PPL	Mustard oil hydrolysis	93% decrease in erucic acid production at 1 g buffer/g oil	[12]
CMC (0.00024 M)	*Rhizopus homothallicus*		70% activity increase	[15]
	Bacillus cereus C₇	Olive oil hydrolysis	50% activity decrease	[17]
0.1% (~0.0015 M)	CAL	*p*-Nitrophenyl palmitate hydrolysis	2.5- and 3-fold activity increase for immobilized and free lipase, respectively	[21]
0.5%, w/v (~0.0075 M)	*Bacillus cereus* C71		60% activity increase	[22]
	Fusarium oxysporum		10% activity increase	[18]
0.0007 M	Kid pregastric lipase	*p*-Nitrophenyl butyrate hydrolysis	100% activity increase	[10]
> CMC (0.00024 M)	CRL		50–60% activity increase	[9]
	CVL, PFL, *Bacillus* sp.		Activity increase by 55%, 70%, and 25%, respectively	[9]
0.001%, w/v (~0.000015 M)	*P. fluorescens* B52		7% activity increase	[9]
	Eukaryotic lipase		60–80% inhibition around CMC	[9]
	Chicken pancreas lipase		Activity decrease	[23]
Triton X-114				
	Fusarium oxysporum		50% activity increase	[18]

also indicate that activities of some lipases (PPL and *Bacillus cereus* C₇) decreased in the presence of most of the nonionic surfactants.

Various groups of researchers compared impacts of Tween- and Triton-type surfactants on the same lipase. Their observations clearly signify that a particular nonionic surfactant augmented catalytic abilities of some lipases but reduced the same for some other lipases. Possibly, lipase–surfactant interaction varies with either type of lipase or that of nonionic surfactant. Polyethylene glycol sorbitan monopalmitate (Tween 40) and Tween 80 inhibited the activity of extracellular, alkalophilic lipase from *Bacillus* sp. LBN2, whereas octylphenoxy polyethoxyethanol (Triton X-100) and polyethylene glycol *tert*-octylphenyl ether (Triton X-114) augmented its activity [24]. Possibly, Triton-type surfactants enhanced the frequency of lipase–substrate contact and also helped lipase to remain in open form. Triton X-100 significantly enhanced the activity of organic solvent-stable *Pseudomonas stutzeri* LC2–8 lipase [25]. Triton X-100 was found to increase the activity of lipase from *Chromohalobacter canadensis* by a greater extent (112%) compared to Tween 80 (65%) and polyethylene glycol sorbitan monolaurate (Tween 20) (38%) [26]. Li et al. [27] noted that in case of *Aureobasidium pullulans* lipase, there was significant augmentation of activity on incorporation of Tween 20 (by 103.9%) and Tween 80 (by 159.6%). Triton X-100 increased it to a low extent (by 12%). Tween 80–activated *Pseudomonas stutzeri* PS59 lipase as conformation of active site became more flexible through lipase–surfactant hydrogen bond formation [28, 29].

Concentrations of nonionic surfactants played a significant role in controlling lipase activity. Studies summarized in Tables 2 and 3 show that almost all the nonionic surfactants increased the catalytic ability of lipase at low concentrations (0.0075 M or lower) but decreased catalysis when used at higher concentrations (0.01 M or higher). Nonionic surfactants, present at low concentrations, could co-adsorb with globular proteins (like enzymes). But, these surfactants displaced protein completely at high concentrations [30]. Tween 80 stimulated lipases at very low concentration (1/100 to 1/10,000 of CMC) [6]. Rise in concentration for all Span-type surfactants (except sorbitan monostearate (Span 60)) augmented the activity of *Bacillus stearothermophilus* MC7 lipase. Tween surfactants at low concentrations (less than CMC) also activated this lipase, possibly by enhancing substrate solubility [31]. High concentrations of nonionic surfactants of polyoxyethylene (1%, *w/v*) or alkylarylpolyoxyethanol (10%, *v/v*) type inhibited triolein hydrolysis by hog pancreas lipase remarkably [32]. Nonionic surfactants like alkyl maltosides and octyl glucosides inhibited *Thermomyces lanuginosus* lipase (TLL) at high concentrations but activated TLL by 10 times at low concentrations, and in both cases, concentration was below CMC [33]. Concentration of Triton X-100 was found to be statistically significant during sardine oil hydrolysis catalyzed by *Cryptococcus* sp. MTCC 5455 lipase [34]. But, there are exceptions also. Catalytic ability of CRL increased in the presence of both high [11, 16] and low [9] concentrations of nonionic surfactants. Low concentrations of polyoxyethylene- (1%, *w/v*) or alkylarylpolyoxyethanol-type nonionic surfactant had no impact on hog pancreas lipase activity. In gum arabic (GA)–stabilized oil-in-water emulsion, a low concentration (< 0.1%) of Tween 80 did not affect free fatty acid (FFA) production from lipid, but FFA production was enhanced as concentration exceeded 0.1% [35]. At certain high concentrations (0.7% and higher), Tween 80 remained attached with lipase and thus displaced GA from the interface. This obstructed interfacial lipase adsorption and decreased its catalytic activity [36].

The interaction between nonionic surfactant and lipase depends on pH also. Mesa et al. [37] observed that on increasing pH, the effect of Triton X-100 on TLL diminished. At pH 5, Triton X-100 had a hyperactivating effect on TLL, and this diminished after 48 h. At pH 7, it had nonhyperactivating effect but stabilized TLL even after 48 h. At pH 9, it had no positive effect on TLL performance. Concentration of a polyethylene glycol dodecyl ether-type nonionic surfactant (Thesit) had a significant effect on *Bacillus subtilis* lipase A, the smallest known lipase. This impact was also controlled by pH, through control of hydrophobic surface area [38].

Some studies revealed another stark fact about effects of surfactants on activities of lipases. Catalytic activity of lipase from one origin was either increased or decreased by all nonionic surfactants of the same type, whereas lipase from another origin was affected in widely different ways by different nonionic surfactants of the same type. *Fusarium oxysporum* lipase was inhibited by all Tween surfactants but was activated by all Triton surfactants [18]. In olive oil hydrolysis, *Rhizopus delemar* lipase (RDL) was completely inhibited by all Tween surfactants (Tween 20, Tween 40, Tween 60, Tween 80). All Span surfactants (Span 20, Span 40, Span 60, Span 80) also decreased its activity [39]. *Geotrichum candidum* lipase and *Candida cylindracea* lipase were inhibited by all surfactants. In case of *Chromobacterium viscosum* lipase (CVL), sorbitan monolaurate (Span 20) increased its catalytic performance highly, Span 80 a little, and sorbitan monopalmitate (Span 40) had no effect, whereas Span 60 decreased it. *Pseudomonas* sp. lipase acted as a completely 1,3-specific lipase in the presence of Tween surfactants. Span 40 was the best for this lipase, Tween 20 enhanced its activity little, but Tween 40, polyethylene glycol sorbitan monostearate (Tween 60), and Tween 80 inhibited it [39].

Water played an important role in controlling the catalytic ability of lipase, particularly in the presence of polyethylene glycol monododecyl ether-type nonionic surfactants. In palm oil transesterification with stearic acid using *Rhizopus* sp. lipase, triethylene glycol monododecyl ether was the best performing nonionic surfactant. In hydrocarbon phase, lipase molecules remained dispersed by hydrated nonionic surfactant and had better access of reactants than in the case involving anionic surfactant like sodium bis(2-ethylhexyl) sulfosuccinate (AOT) [40]. Mole ratio of water to (nonionic) surfactant, i.e., ω_0, was a critical parameter behind hydration of nonionic surfactant. Tetraethylene glycol monododecyl ether ($C_{12}EO_4$) was applied in RDL-catalyzed esterification of hexanol with oleic acid in decane. Extent of esterification was low at low ω_0 (< 5), attained a plateau for intermediate ω_0, and on increasing ω_0 further, increased again [41]. Catalytic performance of *Pseudomonas cepacia* lipase (PCL) was optimum at ω_0 of 8 during esterification of octanol with lauric acid in $C_{12}EO_4$/isooctane microemulsion, as water necessary for hydration of every ethylene oxide group of surfactant was available at that ω_0 [42]. Above this ω_0, shapeless aggregates changed to spherical RMs. Lipase exhibited maximum activity at this structural transition. On increasing ω_0, additional water barrier formed between lipase and micellar interphase. This decreased substrate diffusion and, simultaneously, rate of esterification [43]. Naoe et al. [44] carried out esterification of oleic acid with octyl alcohol catalyzed by RDL in RM of sugar ester DK-F-110. Reaction rate was dependent on ω_0 and DK-F-110 concentration. DK-F-110 RM, with higher turnover number, helped in better catalysis compared to AOT RM. The maximum rate was obtained at a ω_0 of 2.5, pH 6, and 40 °C. The extremely low ω_0 pinpointed that sugar ester RM created a proper hydrophilic environment for catalysis by lipase during esterification molecules. Uehara et al. [45] examined the catalytic ability of RDL during hydrolysis of triolein in a w/o microemulsion consisting of DK-ester-F-110, isooctane, and butanol (a co-solvent). The maximum initial rate was enhanced about 2-fold on addition of butanol. Solubilized water content also had impact on the initial rate of hydrolysis. Sufficient hydrophobicity of water pool and fluidity of microinterface were also necessary for adequate hydrolysis.

A nonionic surfactant named Lutensol AT50 helped PCL to catalyze complete polymerization of pentadecalactone in hexadecane; leading to formation of biodegradable polymer nanoparticles. PCL also successfully catalyzed co-polymerization of pentadecalactone and dodecalactone at low temperature to synthesize noncrystalline polyesters in mini-emulsion of Lutensol AT50 [46].

Catalysis by Free Lipase in Nonionic Surfactant–Formulated Water-in-Ionic Liquid Microemulsions

Nonionic surfactant–formulated water-in-ionic liquid (w/IL) microemulsions can affect the catalytic activity of free lipase substantially. A ternary system with a hydrophobic ionic liquid (IL) named 1-butyl-3-methylimidazolium hexafluorophosphate ((BMIM)(PF_6)), nonionic surfactant (Tween 20 or Triton X-100), and aqueous phase (buffer of pH 7.5) retained the catalytic ability of CRL, CVL, and TLL during esterification of lauric acid with 1-propanol [47]. Variation of catalytic abilities of lipases with ω_0 passed through a maximum. At higher temperature (50 °C), the operational stability of free lipases in this w/IL microemulsion was significantly higher than that of other microheterogeneous systems. Circular dichroism and Fourier transform infrared spectroscopy found that lipase in this microemulsion retained original structure or sometimes attained more robust structure [47]. Lima et al. [48] applied Tween 20 and (BMIM)(PF_6) to prepare w/IL microemulsion-based organogels (MBGs).

Activities of *Candida antarctica* lipase (CAL) and CVL immobilized in these MBGs were up to 4.4-fold higher than water in oil-based MBGs during esterification of lauric acid with butanol. Lipases in w/IL MBGs retained activity for a long time even at 70 °C. The rates and conversions were significantly higher in Tween 20–based w/IL microemulsions than those in AOT-based RM, water-saturated (BMIM)(PF$_6$), and surfactant-free microemulsion-like ternary systems [48]. Commercial CRLs could not effectively catalyze esterification of phytosterols with fatty acid in a conventional reaction system but efficiently catalyzed the same in a w/IL microemulsion containing nonionic surfactant like (BMIM)(PF$_6$)/Tween 20/H$_2$O. These studies clearly show that nonionic surfactant (in particular, Tween 20)–based w/IL microemulsion can act as an effective medium to augment catalysis by free lipase [49].

Nonionic Surfactant Aided Oil Removal by Free Lipase

Triton X-100 enhanced *Penicillium chrysogenum* lipase activity by 50%, while SDS suppressed it during bioremediation of waste cooking oil [50]. Triton X-100 (1%) also increased *Ralstonia pickettii* lipase activity by 30% at pH 7 and 37 °C during removal of oil in laundry. Oil removal increased with an increase in temperature [51]. Lipase from a thermoalkalophilic *Pseudomonas* species was significantly active in the presence of polyethylene glycol sorbitan trioleate (Tween 85), Span 80, and Span 20 during olive oil removal from cotton fabric. As this lipase was stable in high pH and temperatures in the presence of surfactant, it could act as an additive in detergent formulations [52]. A lauryl glucoside-type nonionic surfactant (Glucopone 600 (G600)) was better than ionic surfactants in retaining stability and interfacial adsorption of genetically engineered variants of TLL during fatty soil cleaning [53]. G600 also retained the highest stability of T1 lipase during dishwashing. G600 lowered thermal denaturation and thus helped T1 lipase to express better activity, whereas Tween 80 slightly inhibited this lipase [54]. To the contrary, cleaning of soil involving tributyrin or triolein by TLL was diminished in the presence of commercial nonionic surfactants. Possibly, the lipase–substrate interaction decreased due to surfactant adsorption at the soil surface [55].

Enantioselective Separation Catalyzed by Free Lipase in the Presence of Nonionic Surfactants

Nonionic surfactants had significant impacts on lipase-catalyzed enantioselective separations. Tween 60, Tween 80, and nonyl phenol polyoxyethylene ether (OP-10) stimulated the catalytic ability of crude and purified CRL in enantioselective hydrolysis of 2-chloroethyl ester of ketoprofen. Nearly optically pure (S)-ketoprofen (S-2-(3-benzoylphenyl) propionic acid) with high enantiomeric excess was obtained. Tween 80 (2%, *w/v*) augmented enantiomeric ratio by 5 and 12 times for crude and purified CRL, respectively. OP-10 was even better than Tween 80. At higher concentrations of OP-10, the hydrophobic part of free surfactant moved away from the lipase surface or might form a bilayer around a lipase molecule, leading to lower catalysis by lipase [56]. RDL was the best lipase in increasing enantioselectivity during enantioselective esterification of racemic glycidol with lauric acid in cyclohexane in the presence of dioleyl-*N*-D-glucono-L-glutamate, a nonionic surfactant [57]. In hydrolysis of 2-phenylpropane-1,3-diol diacetate ester using crude PPL, all alkyl (thio)glucoside- and maltoside-type nonionic surfactants reduced conversion but octyl thioglucopyranoside and *n*-dodecyl glucoside augmented enantiomeric excess. All Span surfactants decreased conversion, but Span 80 led to higher enantiomeric excess. Triton X-100 and Triton X-114 reduced

conversion and enantiomeric excess. All polyoxyethylene-type nonionic surfactants decreased conversion, but octyl glycol and octadecyl glycol increased enantiomeric excess [58]. In the transesterification of (RS)-1-phenylethanol with vinyl acetate, *Aspergillus oryzae* lipase, modified by Tween 40, showed high catalytic ability and enantioselectivity for the kinetic resolution of (RS)-1-phenylethanol in the presence of an organic co-solvent of tetrahydrofuran and a phosphate buffer of pH 7.0. (R)-1-phenylethyl acetate was obtained at an enantiomeric excess of more than 99% [59]. These outcomes also made it clear that nonionic surfactant–lipase interaction varies with a type of surfactant. Low concentration of surfactant was generally more effective in enhancing enantiomeric excess.

Effects of Nonionic Surfactants on the Catalytic Performance of Immobilized Lipase

Nonionic surfactants significantly affected activities of immobilized lipase, either being present as a component during immobilization or as a component in reaction medium. Zeta potential analysis showed that the electrostatic interaction between the enzyme and the support for immobilization is critical for high loading density of enzyme through adsorption and covalent bonding [60]. Nonionic surfactants most possibly alter this interaction. Inappropriate immobilization lacks proper orientation for which there can be burial of lid, ultimately leading to a loss of activity. But, surfactants can form an interface which keeps the lid of lipase open. Interfacially activated lipase can be immobilized in such open state, ultimately augmenting the activity [61, 62].

Aspergillus niger lipase (ANL), immobilized on silk fiber, manifested poor catalytic activity during sunflower oil hydrolysis in biphasic oil–water medium, but Triton X-100 augmented its activity significantly [63]. Tween 20, Tween 80, and Triton X-100 augmented the catalytic performance of ANL, immobilized on magnetic nanoparticle, during production of glycerol carbonate [64]. A very small concentration of Triton X-100 (below CMC) greatly enhanced activities of *Pseudomonas fluorescens* lipase (PFL) and CAL immobilized on glyoxyl agarose and cyanogen bromide–activated sepharose. Activity of PFL–glyoxyl agarose increased in the presence of Triton X-100. Increment in the concentration of nonionic surfactant actually diminished lipase activity, even when it was immobilized [21]. The surfactant partly helped to keep lipase in open form, but partial inhibition might also take place due to the competition between substrate and surfactant molecules for the adsorption site of lipase [21]. The presence of Tween 80 during immobilization of CAL B on carboxy-functionalized single-walled carbon nanotubes enhanced the catalytic performance of the lipase during production of biodiesel [65].

CRL, immobilized through adsorption as nanoconjugates on acid-functionalized multi-walled carbon nanotubes, acted as a catalyst for producing methyl oleate ester [66]. Immobilized CRL, in the presence of Triton X-100 and Tween 80, led to the increased extent of esterification when compared with free CRL in the presence of the same surfactants. These nonionic surfactants altered surface charge density at the interfacial region through the hydrophobic modification of CRL and thus assisted immobilized CRL to concentrate at the interface. The hydrophobic surfaces of carbon nanotubes possibly interacted with an amphiphilic alpha-helix peptide covering the active site of CRL; consequently, the stability of open conformation of CRL increased and thus its catalytic ability augmented further [66]. But, Tween 80 and Triton X-100 could not enhance conversion during pentyl valerate synthesis,

catalyzed by CRL immobilized in MBGs. Low ω_0 and weak, fragile MBGs were mainly responsible for the low conversion [67]. Zhang et al. [68] used nonionic surfactants during immobilized CRL (in MBGs)–catalyzed transesterification of 2-phenylethanol with vinyl acetate. Surfactants, working as the interface between buffer and organic phase, acted as the first level of protection to lipase. Surprisingly, the Triton X-100–based MBG was less catalytically active than the AOT-based MBG. Dave and Madamwar [69] observed that nature of co-surfactants and oil-affected CRL-catalyzed esterification of ethyl alcohol with butyric acid in quaternary (Triton X-100/water/1-hexanol/n-hexane) water-in-oil MBG. Esterification increased with increasing ω_0 at constant Z, i.e., (moles co-surfactant)/(moles surfactant). At ω_0 of 30 and Z of 8, 100% esterification was achieved. For several recycles, MBGs were stable and lipase retained its activity. Thermal stability increased five times on immobilization. Tween 80 enhanced the ability of immobilized CRL to produce S-naproxen from enantioselective hydrolysis of racemic naproxen methyl ester [70]. CRL, immobilized on glyoxyl agarose, manifested better catalytic ability in the presence of Triton X-100 [71]. Cross-linked and entrapped CRL manifested eight times higher activity than soluble CRL during esterification of conjugated linoleic acid and ethanol in nonaqueous medium. The MSU-H-type mesoporous silica support was modified by a nonionic surfactant of the triblock co-polymer Pluronic P123 before immobilization. Covalent and noncovalent interactions like electrostatic repulsion and hydrophobic interaction were present between CRL and support, activated by the surfactant [72]. *Rhizomucor miehei* lipase, adsorbed on chitosan beads and subsequently cross-linked with glutaraldehyde, showed excellent catalytic ability and thermal stability even at a higher temperature (60 °C) during synthesis of flavor esters in the presence of Triton X-100 [73]. TLL-magnetic cross-linked enzyme aggregates (mCLEAs) retained activity for a long time on repeated use for more than 4 weeks [74]. The addition of Tween 80 (0.0006 M) to the TLL-mCLEA system enhanced the yield of biodiesel by 1.5 times, and stability and reusability were also high. Surfactant-activated TLL-mCLEA manifested high activity, improved stability, and high reusability. Yang and Zhang [75] observed that *Burkholderia cepacia* lipase (BCL), when pretreated with 0.0001 M Triton X-100 and subsequently immobilized in mCLEAs with hydroxyapatite-coated magnetic nanoparticles, experienced a maximum increase in activity (~ 15%), whereas small activity enhancement (~ 5%) was achieved with 0.0002 M Tween 80. Nonionic surfactant during pretreatment possibly fixed BCL with its lid open and thus enhanced its activity, ultimately facilitating biodiesel production in solvent without further addition of water. Catalytic performance of immobilized (cross-linked) and nonionic surfactant (Tween 80 or Triton X-100)–pretreated *Rhizopus oryzae* lipase (ROL) during esterification was better than that of free lipase and nonpretreated, immobilized lipase. In terms of pretreating ability, Tween 80 was better than Triton X-100 [61]. Liu et al. [62] synthesized a novel immobilized lipase from *Yarrowia lipolytica* lipase LIP2, covalently immobilized on functionalized Fe_3O_4 magnetic nanoparticles (MNPs) in RM. The addition of Span 20 lifted catalytic activity by 12 times. At high ω_0, excess water led to loose lipase structure and ultimately diminished its catalytic ability [76]. Nonionic colloidal liquid aphron (CLA) formulated by ANL with 1% Tween 80/mineral oil and 1% Tween 20 increased its catalytic ability by 7 times. Changes in the Michaelis–Menten constant (K_m) of lipase supported the fact that immobilization led to large conformational changes [77]. Sánchez-Otero et al. [78] immobilized *Geobacillus thermoleovorans* CCR11 lipase on porous polypropylene, a hydrophobic support, by adsorption. Immobilization with Triton X-100 augmented the reusability and activity of lipase, possibly due to breaking of protein (enzyme, i.e., lipase) aggregates and/or stabilization of an open form of lipase [21]. But, Pencreac'h et al.

[79] noticed that PCL, immobilized on polypropylene, lost its activity totally after 10 min of exposure to 0.4% Triton X-100. This difference clearly points out that the hydrophobic interaction between the *Geotrichum thermoleovorans* lipase and the polypropylene support was strong. Another study observed a similar change in lipase activity [80]. The presence of Triton X-100 during immobilization of TLL on polypropylene doubled activity retention even after 30 h at 50 °C. Lipase immobilized without Triton X-100 showed better thermal stability, probably due to the presence of oligomers and other lipase aggregates [81]. The difference in catalytic abilities of various immobilized lipases in the presence of the same surfactant (Triton X-100) emphasized that the type of lipase controlled the lipase–surfactant interaction even in its immobilized state. Triton X-100 somewhat modified dependence of thermal stability on immobilization, as increasing temperature decreased activity further. Zhao et al. [82] applied a nonionic surfactant for interfacial activation of ROL, after which it was immobilized on nanoparticle of Fe_3O_4, previously modified by 3-aminopropyltriethoxysilane (APTES) and glutaraldehyde. Sucrose esters-11 worked better than other nonionic surfactants like Tween 20, Tween 60, Tween 80, Triton X-100, and sucrose esters-15 as activator. Immobilized ROL had hydrolytic activities 9.16 times and 31.6 times that of free lipase with *p*-nitrophenyl butyrate and *p*-nitrophenyl palmitate, respectively, as substrates. Its specific esterification activity was also 1.5 times that of free lipase. It had higher thermostability than free lipase. On increasing concentration of sucrose esters-11, lid of lipase opened more and the activity increased. Zhao et al. [83] immobilized ROL, interfacially activated by Tween 80, modified by APTES and glutaraldehyde, on nanoparticle of Fe_3O_4. This immobilized ROL had specific hydrolytic and esterification activities 16.6 and 2.6 times that of free ROL.

Catalysis by Nonionic Surfactant–Coated Lipases

Stability and simultaneous catalytic activity of lipase remain quite low in organic solvents due to partial deactivation. Coating by surfactant prevents this deactivation and enhances the solubility of lipase in organic solvents [84]. Nonionic surfactants might shift equilibrium of lipase towards open conformation by coating the hydrophobic area surrounding its active site [85]. High reaction rate and no necessity to control water content in organic media are advantages of surfactant-coated lipase (SCL) system [84]. SCL acted better than AOT-isooctane RM, two-phase isooctane–water system, and isooctane–powder lipase system. The activity of SCL, comprising of nonionic surfactants, depended strongly on the structure of the hydrophobic part of surfactant. SCL from nonionic surfactant having two hydrocarbon chains like glutamic acid dioleyl ester ribitol amide ($2C_{18}\Delta^9GE$) performed better than SCL from nonionic surfactant having one hydrocarbon chain ($1C_{18}\Delta^9GE$) [86]. SCL having more hydrophobic groups was more soluble in organic solvent, and this probably led to such observation [85].

In general, the molecular structure of the hydrophilic part of surfactant has great effect on the activity of SCL [85]. Naturally, SCLs having different nonionic surfactants will manifest a wide variation in their catalytic abilities. Table 4 describes the performance of lipases coated with $2C_{18}\Delta^9GE$, the most extensively used coating surfactant. CRL coated with $2C_{18}\Delta^9GE$ showed a remarkable increase in catalytic ability during methyl ester formation from Chinese tallow kernel oil [87], olive oil hydrolysis [88, 89], and esterification [90]. Lipases (ANL, *Pseudomonas* sp., *Rhizopus* sp., and *Mucor javanicus*) showed significant activity enhancement when coated with $2C_{18}\Delta^9GE$ during resolution of racemic menthol [91] and esterification of lauric acid with benzyl alcohol [92].

Table 4 Performance of surfactant-coated lipase (SCL) prepared with glutamic acid dioleyl ester ribitol amide ($2C_{18}\Delta^9GE$)

Source/type of lipase	Details of reaction	Effects on conversion and lipase activity	Reference
CRL	Chinese tallow kernel oil to fatty acid methyl ester	93.86% conversion in 9.2 h at 49 °C, 18.5% SCL, 3:1 methanol-to-oil ratio and 15.6% water	[87]
CRL	Olive oil hydrolysis in hydrophilic polyacrylonitrile hollow fiber membrane reactor	Conversion doubled compared to native lipase pre-immobilized on membrane	[88]
CRL	Olive oil hydrolysis in organic-aqueous 2-phase system	SCL having 1.8 times higher activity than native lipase; $(K_m)_{SCL} = 0.5 \times (K_m)_{native\ lipase}$; $(V_{max})_{SCL} = 2.4 \times (V_{max})_{native\ lipase}$	[89]
CRL	Esterification of lauric acid with lauryl alcohol	SCL better than AOT/isooctane RM	[90]
CRL, *Mucor javanicus*	Resolution of racemic ibuprofen, 2-(4-isobutylphenyl) propionic acid, through enantioselective esterification with fatty alcohol	100 times higher reaction rate for SCLs than powder lipase in isooctane; CRL was better	[84]
ANL, CRL, PPL, *Rhizopus* sp., *Pseudomonas* sp., *Mucor javanicus*	Resolution of racemic menthol through enantioselective esterification with lauric acid	90% of (−)-ester and 9% of (+)-ester in 24 h at 35 °C; 100 times higher rate for SCL than powder lipase	[91]
ANL, CRL, *Pseudomonas* sp., *Rhizopus* sp., *Mucor javanicus*	Esterification of lauric acid with benzyl alcohol	SCL was more thermostable, better than AOT RM and isooctane–powder lipase system; no reaction by native lipase from ANL and *Rhizopus* sp., but SCLs catalyzed reaction	[92]

Table 5 [93–99] describes the performance of lipase coated with Span-type surfactants. Span 60 was the preferred coating surfactant in most of the studies. It augmented catalytic abilities of lipases like CRL and *Rhizopus japonicus* lipase. In a stunning observation, *Pseudomonas* sp. lipase coated with Span 60 showed much higher activity in ethanol than in water [97]. The same SCL efficiently catalyzed esterification, whereas crude lipase in the presence and in the absence of surfactant showed no activity [98].

Catalysis by Nonionic Surfactant–Coated Lipases Immobilized on Specific Supports

CRL, coated with surfactant and immobilized on GA-coated magnetic nanoparticles of ferrosoferric oxide, acted as a biocatalyst for ethyl isovalerate (a flavor ester) synthesis [85]. Lipase coated with 1 mM Triton X-100 resulted in much better esterification compared to lipase coated with cationic (cetyltrimethylammonium bromide (CTAB)) and anionic (AOT) surfactants. Magnetic support material kept lipase activity constant by retaining exact amount of water. The surface of GA might interact with the surface of lipase coated with nonionic surfactant, leading to enhanced rate of esterification. Catalytic performance of the SCL was constant even after the seventh recycle [85]. CRL coated with Tween 80 and immobilized in microemulsion of Triton X-100–based organogels outperformed the same SCL, immobilized in CTAB- and AOT-based organogels and uncoated lipase [100].

Table 5 Performance of surfactant-coated lipase (SCL) prepared with Span surfactants

Source/type of lipase	Surfactant	Details of reaction	Effects on conversion and lipase activity	Reference
Rhizopus japonicas lipase	Span 60	Interesterification of tripalmitin and stearic acid in *n*-hexane	SCL was active, whereas crude lipase had no activity; pH and surfactant/lipase ratio had significant impact on rate	[93]
CRL	Span 60	Tuna oil hydrolysis in aqueous-organic system	$(K_m)_{SCL} = 0.5 \times (K_m)_{native\ lipase}$; $(v_{max})_{SCL} = 11.5 \times (v_{max})_{native\ lipase}$; enrichment in triglyceride mixtures: docosahexaenoic acid from 19.1 to 38.9%, eicosapentaenoic acid by 1.5 times	[94]
CRL	Span 60	Esterification of (−)-menthol and (±)-menthol with lauric acid	SCL increased conversions from 23 to 94% of (−)-menthol in 4 h; from 19 to 62% of (±)-menthol in 6 h	[95]
Rhizopus japonicus	Span 60	Esterification of lauric acid and dodecyl alcohol	SCL more stable than crude lipase; activity highest in the absence of external water, rate increased up to 45 °C	[96]
Pseudomonas sp.	Span 60	Palm oil hydrolysis	SCL with ethanol 35 times more active than SCL with water	[97]
Pseudomonas sp.	Span 60	Esterification of palmitic acid with cetyl alcohol, methanol, monoacylglycerol, diacylglycerol, and triacylglycerol (all in *n*-hexane)	Efficient catalysis by SCL, whereas no reaction by crude lipase and crude lipase with surfactant	[98]
ANL, CRL, PPL	Span 85 (sorbitan trioleate)	Esterification of geraniol with acetic acid	3.28-, 72.3-, and 6.24-fold greater conversion, respectively, compared to crude lipases; for CRL, yield much higher than RM and crude lipases	[99]

CRL, coated with surfactant and immobilized on silica, catalyzed ethyl butyrate (a flavor ester) production also [101]. Triton X-100 was better than Tween 80 as a coating surfactant. But, in another study [102], Tween 80 was found as the best surfactant in coating CRL, which was subsequently immobilized in sol–gel supports for transesterification of sucrose with acetic acid to produce sucrose-6-acetate. At elevated temperatures, SCL immobilized in sol–gel was more catalytically active than free CRL, CRL immobilized in sol–gel, and SCL without

immobilization. Coating followed by immobilization protected lipase effectively against thermal denaturation. Conformational limitation on the enzyme movement, due to electrostatic interaction and enzyme–support hydrogen bonding, and low restriction in substrate diffusion at high temperature could be possible reasons behind such improvements.

Catalysis by Nonionic Surfactant–Coated Lipases in Organic Solvents

SCLs prepared with nonionic surfactants often showed sensitivity to organic solvents. BCL, coated with propylene glycol monostearate (a nonionic surfactant), catalyzed production of ascorbyl palmitate in the presence of molecular sieves [103]. The SCL was completely inactive in methanol, hexane, acetone, chloroform, and isopropanol but was active in *tert*-butanol. Unlike most of the organic solvents, *tert*-butanol did not strip essential water molecule bound to lipase, rather the microaqueous environment around it augmented stability. Temperature had a profound effect on the catalytic activity of SCL in organic solvents. At optimum temperature (50 °C), SCL was 8 times more active compared to free lipase [103]. Nonionic surfactant–coated RDL showed high stability and activity in hydrophobic organic solvents, but no activity in halogenated solvents [104]. SCL from RDL and *Pseudomonas fragi* 22-39B lipase (PFRL) catalyzed diacylglycerol and triacylglycerol syntheses from monoacylglycerols and aliphatic acids in homogeneous and dry benzene assisted by molecular sieves. SCL from PFL was more thermostable than free lipase and catalyzed ester exchange reactions in organic solvents containing a very low amount of water (250 ppm), but no reaction occurred in dry organic solvents [77]. PFRL, coated with synthetic nonionic surfactant didodecyl *N*-D-glucono-L-glutamate, worked better than SCLs from *Pseudomonas* sp., *Penicillium roqueforti*, *Pseudomonas niger*, and RDL for hydrolysis of lipophilic esters in an aqueous-organic system. The extent of reaction increased with increasing aqueous phase volume but was independent of its pH. So, hydrolysis definitely occurred in organic phase with water molecules coming from aqueous phase. SCL from PFRL was the best for esterification of triglyceride and enantioselective esterification of 1-phenylethanol also [105]. PFRL, coated with a dialkyl nonionic surfactant, esterified racemic alcohols with excess aliphatic acids enantioselectively in various relatively dry organic solvents (40–80 ppm water) in the presence of molecular sieves [106]. Rate increased with increasing alkyl chain length, but high enantioselectivity was obtained with hexanoic and dodecanoic acids. PCL, coated with $2C_{18}\Delta^9GE$, enhanced conversion of pentadecalactone during polymerization by 10 times. This SCL led to a higher molecular weight of polymer and was a better catalyst for ring-opening polymerization due to its higher solubility in organic solvent, compared to uncoated lipase [107].

Summary

Formation of micelle by surfactants, concentrations of free and micellar substrate, and their availability to lipase made the interactions among lipases, substrates, and surfactants quite complex. The hydrophobic as well as hydrophilic part of surfactant played a distinct role in such interactions. Low concentration of nonionic surfactants mostly stabilized lipase through hydrophobic interactions and enhanced substrate solubilization. This ultimately augmented the catalytic ability of lipase. But, at higher concentration, nonionic surfactants often decreased rate of reaction by solubilizing substrate in micelles of excess surfactant, thus reducing effective substrate concentration in interfacial region (the working zone for lipase). Lipase displacement

from the interface at high surfactant concentration also led to reduced catalysis. In GA-stabilized emulsions, this trend was somewhat opposite. The pH of reaction medium has the potential to alter the interaction between nonionic surfactant and lipase. The presence of Tween surfactants changed positional specificity of *Pseudomonas* sp. lipase from nonspecific to completely 1,3-specific. Alteration of the electrostatic interaction between lipase and immobilization support by nonionic surfactant increased the activity of some immobilized lipases, where the surfactant was used either as a component in reaction medium or as a component in immobilization support. PPL showed enhanced activity when immobilized on ordered mesoporous silica, prepared using a nonionic surfactant. Tween 80, Triton X-100, and Span 60 were responsible in augmenting enantiomeric separation catalyzed by CRL, *Pseudomonas* sp. lipase, etc. Among various lipases, only CRL always showed higher catalytic ability in the presence of Span, Tween, and Triton surfactants. So, this lipase can be a good choice in future studies. Denaturation of lipase in organic solvents could be resisted by coating it with nonionic surfactant like $2C_{18}\Delta^9GE$ and Span surfactants. So, nonionic surfactant–coated lipase can be considered as a better catalyst in comparison with free lipase in organic solvents. Lipase coated with nonionic surfactant and then immobilized on supports like magnetic nanoparticles, microemulsion-based organogels, and silica also acted as better catalysts compared to free lipase.

Compliance with Ethical Standards

Conflict of Interest   The authors declare that they have no conflict of interest.

Symbols and Abbreviations   *ANL, Aspergillus niger* lipase; *AOT,* Sodium bis(2-ethylhexyl) sulfosuccinate; *BCL, Burkholderia cepacia* lipase; *(BMIM)(PF$_6$),* 1-Butyl-3-methylimidazolium hexafluorophosphate; *$2C_{18}\Delta^9GE$,* Glutamic acid dioleyl ester ribitol amide; *$C_{12}EO_4$,* Tetraethylene glycol monododecyl ether; *CAL, Candida antarctica* lipase; *CLA,* Colloidal liquid aphron; *CMC,* Critical micellar concentration; *CRL, Candida rugosa* lipase (formerly, *Candida cylindracea* lipase); *CTAB,* Cetyltrimethylammonium bromide; *CVL, Chromobacterium viscosum lipase; FFA,* Free fatty acid; *GA,* Gum arabic; *IL,* Ionic liquid; *K_m,* Michaelis–Menten constant; *MBG,* Microemulsion-based organogel; *mCLEA,* Magnetic cross-linked enzyme aggregate; *OP-10,* Nonyl phenol polyoxyethylene ether; *PCL, Pseudomonas cepacia* lipase; *PFL, Pseudomonas fluorescens* lipase; *PFRL, Pseudomonas fragi 22-39B* lipase; *PPL,* Porcine pancreas lipase; *RDL, Rhizopus delemar* lipase; *RM,* Reverse micelle; *ROL, Rhizopus oryzae* lipase; *SCL,* Surfactant-coated lipase; *SDS,* Sodium dodecyl sulfate; *Span 20,* Sorbitan monolaurate; *Span 40,* Sorbitan monopalmitate; *Span 60,* Sorbitan monostearate; *Span 80,* Sorbitan monooleate; *TLL, Thermomyces lanuginosus lipase; Tween 20,* Polyethylene glycol sorbitan monolaurate; *Tween 40,* Polyethylene glycol sorbitan monopalmitate; *Tween 60,* Polyethylene glycol sorbitan monostearate; *Tween 80,* Polyethylene glycol sorbitan monooleate; *Triton X-100,* Octylphenoxy polyethoxyethanol; *Triton X-114,* Polyethylene glycol *tert-octylphenyl ether*; *V_{max},* Maximum rate of reaction; *ω_0,* (Moles water)/(moles surfactant); *w/IL,* Water-in-ionic liquid; *Z,* (Moles co-surfactant)/(moles surfactant)

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