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Study of the reaction mechanism of the transesterification of triglycerides catalyzed by zinc carboxylates

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ABSTRACT

In this theoretical and experimental study, the mechanisms for the transesterification of triglycerides catalyzed by zinc carboxylates were analyzed and discussed. Different alternatives were examined: (A) the classic Lewis acid mechanism involving the coordination of the triglyceride through the carbonyl group with the Zn^{2+} ion, (B) the coordination of methanol with the Zn^{2+} followed by carboxylate shift, and (C) the co-coordination of methanol and the triglyceride with the Zn^{2+} ion. The preferred mechanism included the initial coordination of methanol, carboxylate shift and the co-coordination of the triglyceride with an alkoxide-like moiety.

The fatty acid esterification reaction catalyzed by zinc carboxylates was also studied. The anion exchange between the carboxylate in the Zn salt and the fatty acid to be esterified was analyzed.

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1. Introduction

The sustainable diversification of energy sources is the new industrial challenge. Renewable energies make up the industrial sector with the greatest growth in the world. The synthesis of biodiesel (FAME, fatty acid methyl esters) from renewable biological sources, including animal fats and vegetable oils, has received considerable attention due to its environmental advantages and sustainable production in comparison with fossil fuels.

In general, almost all biodiesel is produced by transesterification of triglycerides of refined oils with methanol in the presence of a homogeneous base catalysis (NaOH, KOH or $NaOCH_3$) [1]. For low-cost raw materials with high levels of free fatty acids (FFA) and water, a homogeneous acid-catalyzed esterification stage prior to transesterification is necessary.

An important goal in this issue/subject is to find a catalyst able to promote the transesterification of triglycerides and FFA esterification. This catalyst should be easily separated from the reaction mixture and environmentally friendly. In a previous work [2], we found that zinc carboxylate salts of different chain lengths, $Zn(C_nH_{2n+1}COO)_2$ with $n = 11, 15$, and 17 (zinc(II) laurate, palmitate, and stearate, respectively), were active and stable in the transesterification of soybean oil at 100 °C. At temperatures higher than 100 °C, the Zn salts transformed into Zn glycerolate. It was also observed that, in the presence of fatty acids, the carboxylate groups of the salts were gradually exchanged for the carboxylate groups of the carboxylic acid to be esterified [3]. These zinc salts are crystalline solids at room temperature, but soluble in the reaction medium at 100 °C. They re-crystallize rapidly at room temperature.

The literature is not extensive on the issue, but many studies have been reported on the use of zinc as a Lewis acid catalyst in transesterification reactions. Abreu et al. [4] reported that tin, lead, mercury and zinc (3-hydroxy-2-methy-4-pyrone)$_2$(H_2O)$_2$ complexes were active in the transesterification of soybean oil with methanol, with the following order in decreasing activities: $Sn^{2+} \gg Zn^{2+} > Pb^{2+} \approx Hg^{2+}$. For the Zn complex, the maximum FAME yield was 38% after 6 h of reaction at 60 °C. Later, the same catalysts [5] were tested in the transesterification of different alkyl-chain triglycerides and alcohols. For linear alcohols, the reaction activities decreased with increasing hydrocarbon chain length. It was also shown that catalytic activity was higher when vegetable oils with short/medium chain or highly unsaturated fatty acids and short and linear chain alcohols were used.

Di Serio et al. [6] reported on the synthesis of biodiesel using acetates and stearates of Ca, Ba, Mg, Cd, Mn, Pb, Zn, Co, and Ni as catalysts in the transesterification of soybean oil with methanol. At 200 °C, the activity order for stearate salts was: Pb > Cd > Mn > Zn, and for acetate salts: Cd > Pb > Zn = Mn. At 150 °C, the conversion of glyceride groups by zinc acetate was lower than 10%. The authors indicated that the activities could be correlated with the cation acidity.

Hou et al. [7] studied the transesterification and esterification of high FFA oil in subcritical methanol (2 MPa, 180 °C) via Lewis acid catalysts such as $Pb(OOCCH_3)_2$, $Cd(OOCCH_3)_2$ and $Zn(OOCCH_3)_2$.

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Table 1
Characterization of the Zn salts.

Zinc salt	Sample name		Molecular weight (g/mol)	Melting point[a] (°C)	Basal spacing[b] (Å)
$Zn(CH_3COO)_2(H_2O)_2$	Zn acetate	ZnAc	219.4	237	7.1
$Zn(C_{11}H_{23}COO)_2$	Zn laurate	ZnLa	463.6	130	32.2
$Zn(C_{15}H_{31}COO)_2$	Zn palmitate	ZnPa	575.7	130	37.2
$Zn(C_{17}H_{35}COO)_2$	Zn stearate	ZnSt	631.7	130	40.0

[a] Refs. [15,16].
[b] XRD.

For zinc, the results showed an esterification conversion of 96%, and the transesterification conversion reached 69% with soybean oil as feedstock.

Recently, new zinc(II) compounds containing functionalized Schiff bases were studied in the transesterification of soybean oil (150 °C). Their activity could be modulated by the selection of the anions and/or the substituents on the ancillary bidentate ligand [8]. The most active complex was that with acetate as anion. The explanation of this finding would be that a strong Lewis base competed with the substrate in the coordination to the metal site, whereas a weak donor excessively enhanced the acidity of the metal center. Deactivation of the highly acidic metal center through the strong coordination of the product is a probable secondary reaction.

The transesterification of triglycerides consists of three consecutive, reversible reactions. It was proposed in the literature [9–11] that when the reaction is catalyzed by a Lewis acid (specifically a divalent metal complex), the carbonyl oxygen is attacked by the Zn^{2+} cation. This originates an increase in the electrophilicity of the adjacent carbon, making it susceptible to nucleophilic attack. The hydroxyl group in methanol attacks the carbonyl group, resulting in a four-center transition state. The transition state, with the separation of the Zn^{2+} ion from the carbonyl group, originates FAME and diglycerides. Zn^{2+} as a Lewis active site can be active in transesterification reactions in a wide temperature range.

Other mechanisms have been proposed. Abreu et al. [5] and Suarez [12,13] hypothesized that the complex was activated by the reaction with an alcohol molecule, forming a species with a vacant site. Subsequently, the carbonyl group of the ester of the triglyceride coordinates at a vacant site in the catalytic active species. This coordination increases the polarization of the carbonyl, enhancing the nucleophilic attack by the alcohol via a four-member ring transition state.

The goal of the present work was to explore potential answers to the following questions: What is the mechanism for the transesterification of triglycerides catalyzed by zinc carboxylates: the classic Lewis acid mechanism, through coordination of an alcohol with the zinc, or some other pathway reaction? Does the classic mechanism proposed in the literature take place, or are there alternative paths? What is the coordination geometry of zinc during the transesterification reaction: tetra-coordinated, penta-coordinated or multi-coordinated?

In addition to the questions presented above, we were also interested in other topics related to esterification, such as:

- Is it possible to exchange short-chain fatty anions of the carboxylate salt (i.e. zinc acetate) for long-chain fatty acids (i.e. oleic acid) and to generate in situ new carboxylate salts (i.e. zinc oleate) and short fatty acids (i.e. acetic acid)?
- Is there a preference for a certain chain length of the carboxylate generated in situ? Are the type of carboxylate salt and the temperature relevant?

It is important to highlight that zinc is the second most abundant transition element in biology and the only metal known to be represented in enzymes from each one of the six classes established by the International Union of Biochemistry and Molecular Biology [14]. Its flexible coordination geometry, fast ligand exchange, the lack of redox activity, and its role as a Lewis acid are just some of the features that make zinc an invaluable element in biological catalysis.

In this study, the mechanisms for the transesterification of triglycerides and fatty acid esterification reactions catalyzed by zinc carboxylates were examined and discussed considering Zn enzyme performance, mechanisms and Zn chemistry in similar reactions. Experimental results of transesterification and esterification reactions with zinc carboxylate salts are also presented and analyzed.

2. Experimental

2.1. Catalyst preparation

The synthesis of zinc carboxylates ($Zn(C_nH_{2n+1}COO)_2$ with n = 11, 15 and 17) was carried out in an alcoholic solution [15]. The corresponding fatty acid (palmitic and lauric acid from Fluka, stearic acid from Sigma Aldrich, all 99%) and NaOH (Cicarelli, 97%) were mixed in stoichiometric amounts at 40 °C with constant magnetic stirring. Then $ZnCl_2$ (Biopack, 99%) was added dropwise. The obtained precipitate was filtered, washed with deionized water and dried for 12 h at 50 °C. Zinc acetate dihydrate (99%) was obtained from Sigma–Aldrich. The synthesized samples, their names and structural properties are presented in Table 1.

2.2. Catalyst characterization

Catalysts were identified and studied by X-ray diffraction (Philips PW1710, using Cu Kα radiation scan in a 2θ range of 2–60°) and by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS, Nicolet 6700FT-IR spectrometer). The catalysts were mixed with KBr and the IR spectrum was recorded in the 400–4000 cm^{-1} range.

2.3. Anion exchange in Zn carboxylate in the presence of fatty acid

The behavior of the Zn salts in the presence of carboxylic acids with different carbon chain lengths was studied according to Table 2, at 20, 60 and 100 °C, with the same concentrations as used in the esterification reaction (6 wt.% with respect to carboxylic acid) [2].

2.4. Catalytic tests

The catalyst tests were carried out in a 600 cm^3 Parr reactor operated in batch mode, with an agitation rate of 500 rpm. Reactions were studied at 100 °C, with a reaction time of 2 h. The

Table 2
Zn carboxylates experimental reactions with fatty acids.

Catalyst	Carboxylic acids	
	Long chain	Medium/short chain
Long-chain carboxylic anion	ZnSt/oleic acid	ZnOl/lauric acid
Medium-chain carboxylic anion	ZnLa/oleic acid	ZnLa/acetic acid

methanol/oil molar ratio was 30:1, and the catalyst loading was 3 wt.% (with respect to oil).

The acid soybean oil (10 wt.% stearic acid), the methanol and the catalyst were fed into the reactor and then the system was heated up until reaction temperature was reached. At that moment, a zero time sample was taken and the reaction time started. The chromatography of the raw materials and products was carried out according to the standard UNE-EN 14105 norm.

The triglyceride conversion (X_{TG}) and FAME yield (Y_{FAME}) were calculated using the following equations:

$$X_{TG} = \frac{\text{mol TG}_{t_0} - \text{mol TG}_{t_f}}{\text{mol TG}_{t_0}} \quad (1)$$

$$Y_{FAME} = \frac{\text{mol FAME}_{t_f}/3}{\text{mol TGE}_{t_0}} \quad (2)$$

where TGE is the molar equivalent of triglyceride,

$$\text{mol TGE}_{t_0} = \text{mol TG}_{t_0} + \tfrac{2}{3}\text{mol DG}_{t_0} + \tfrac{1}{3}\text{mol MG}_{t_0} + \tfrac{1}{3}\text{mol FFA}_{t_0} \quad (3)$$

3. Theoretical method and approach

The Molecular Mechanics version 2 (MM2) implemented in Chem3D Ultra 5.0 (from Cambridge Soft) was used to obtain the conformational steric minima for each initial configuration explored. For better visualization, ChemBioOffice 2008 was used. After the minimization step, PM3 (parameterized model 3) calculation was performed to obtain the formation ΔH° for each conformational minimum. The reported ΔH° in Tables 5–10 were obtained as follows:

$$\Delta H^\circ = \Delta H_{\text{conformers}}{}^\circ$$

This ΔH° is the standard formation enthalpy for the particular conformation obtained after a step of minimization, and it is obtained from the PM3 calculation.

The calculations of the minimum energy conformation were obtained in two different ways: by minimizing the steric energy (MM2) and by a minimization using the PM3 program itself.

Triacetin was chosen as a triglyceride model compound. This molecule is a practical model compound for the computational study of FAME formation due to its small number of atoms. It was used as a model compound in recent experimental [17–20] and theoretical [21,22] investigations of acid- and base-catalyzed methanolysis for biodiesel synthesis.

3.1. An explanation of the theoretical antecedents of the present study

A comparison of the energies of zinc(II) alkoxides and zinc(II) hydroxides reveals that zinc(II)-alcohol is more easily deprotonated than zinc(II)-water, indicating that a zinc(II)-coordinated alcohol has a lower pK_a than a zinc(II)-coordinated water in the same molecular conformation [23]. For the first time, the study by Tang et al. [23] clearly showed that the zinc(II)-alcoholic OH is a better model for hydrolytic zinc enzymes (having stronger acidity and better nucleophilicity). The analysis of the transition state in the transformation reaction from zinc(II) hydroxide species to zinc(II) alkoxide species indicated that zinc(II) alkoxides are the preferred deprotonated species thermodynamically and kinetically. The zinc(II) alkoxide promoted the transesterification path and the zinc(II) hydroxide promoted the hydrolysis reaction.

In line with these results, Kowalski et al. [24] showed that the mechanism of polymerization of cyclic esters with zinc octoate as catalyst has an initiation step that involves the conversion into the alkoxide derivative. After this first step, a second step takes place and a full zinc alkoxide is generated. The third step (and first propagation) implies the terminal ester formation.

Zn binding sites in proteins can be: (1) sites that play predominantly catalytic roles, and (2) sites that have only a structural role. The best studied "structural" Zn-proteins are those of the Zn-finger family. These proteins are involved in nucleic acid binding and gene regulation. In enzymes, Zn is usually tetrahedral, but it can also adopt a 5- or 6-coordinate geometry, whereas in aqueous solution it is hexa-coordinated. A survey of Zn proteins in the Protein Data Bank shows that for structural binding sites the ratio of tetra/penta/hexa-coordinated Zn is 79:6:12%, whereas for catalytic sites the ratio is 48:44:6%, respectively. The metal coordination number in a given complex is governed by: (1) the dielectric medium or solvent accessibility, (2) properties of the metal (mainly by its ability to accept charge from its ligands), and (3) the chemical characteristics of the ligands. Theoretical studies dedicated to assess the role of non-aqua ligands on the geometry of zinc complexes are scarce.

The reaction medium studied in the present work in the case of transesterification consists of vegetable oil (mainly triglycerides) and methanol, with a reaction temperature in the range from 100 to 140 °C. Methanol is present in higher relative concentration with respect to the oil (methanol:oil molar ratio = 30:1). Therefore the zinc carboxylate interacts with two very different molecules in nucleophilicity and steric hindrance to (potential) coordination to zinc. The triglyceride is, without doubt, more sterically hindered than methanol.

3.2. Transesterification reaction

The transesterification of triglycerides consists of three consecutive, reversible reactions that produce glycerides and FAME:

$$TG + CH_3OH \leftrightarrow FAME + DG$$

$$DG + CH_3OH \leftrightarrow FAME + MG$$

$$MG + CH_3OH \leftrightarrow FAME + G$$

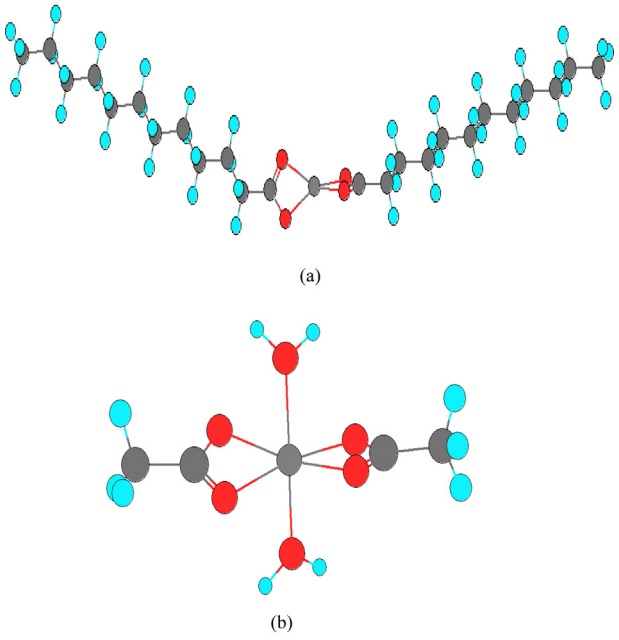

Fig. 1. Scheme of (a) tetrahedral zinc laurate and (b) octahedral zinc acetate.

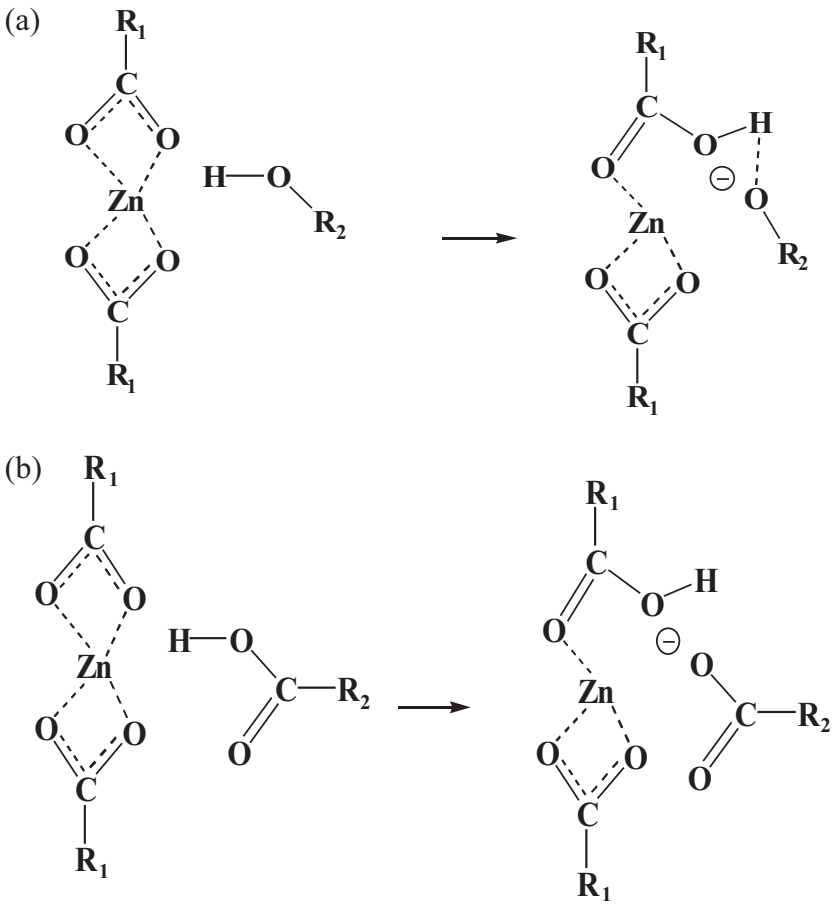

Fig. 2. Carboxylate shift reaction in zinc carboxylate with an alcohol (a) and a fatty acid (b).

where TG, DG, MG, and G are triglyceride, diglyceride, monoglyceride and glycerol, respectively. The reaction products are increasingly more polar in the trend TG < DG < MG < G.

The present study only considers zinc laurate and zinc acetate as catalyst models of medium and short carboxylate salts. Zinc is tetrahedral in the first molecule (Fig. 1a), and when two water molecules are included, such as in zinc acetate, the structure is octahedral (Fig. 1b).

Sousa et al. [14] analyzed a very interesting mechanistic phenomenon known as the carboxylate shift. This is a change in the coordination of a carboxylate group related to a central Lewis acid site. A carboxylate shift is supposed to occur in the first methanol coordination (Fig. 2a). This mechanism allows a virtually constant coordination of zinc during the reaction (four ligands coordinated and a fifth one at a longer coordination length, even for intermediates). Fig. 2b shows the carboxylate shift reaction in zinc carboxylate with a fatty acid.

Three mechanisms are analyzed and discussed:

Mechanism 1: the classic Lewis acid mechanism with the triglyceride (triacetin in this case) coordination through the carbonyl group to the Zn^{2+} ion as the first and main step (Fig. 3a).

For Mechanism 1, the following steps were considered:

Step 1: coordination of triacetin with ZnLa.
Step 2: formation of C—O alkoxide from polarization of the C=O of the triacetin.
Step 3: formation of alkoxide through interaction of methanol with polarized C—O of triacetin.
Step 4: generation of methyl acetate and diglyceride, regeneration of carboxylate salt.

The classic Lewis acid mechanism excludes the carboxylate shift step and always includes a penta-coordinated zinc, but there is a whole side of the zinc salt that is "empty" (as shown in Fig. 3b). It does not seem logical that, with a Lewis acid ion such as Zn^{2+}, no coordination with the "empty" side of the molecule takes place when methanol and triglycerides are present. Moreover, the other mechanistic steps exclude the direct coordination of the methanol to the ion because the reaction is believed to occur through the polarized C—O bond of the carbonyl group.

Mechanism 2: the coordination of methanol and its reaction with the formation of alkoxide group linked to Zn^{2+} as the first step, and through the carboxylate shift the change of status of one of the carboxylate moieties (linked to Zn^{2+} by ionic charges) to carboxylic acid (linked to Zn^{2+} by Van der Waals forces through the O of the C=O) (Fig. 4).

For Mechanism 2 the following steps were considered:

Step 1: coordination of methanol with ZnLa.
Step 2: formation of Zn—OCH_3 bond and carboxylate shift, generation of carboxylic acid coordinated with Zn^{2+}.
Step 3: polarization of C=O of triacetin adsorbed onto methoxide.
Step 4: generation of methyl acetate and diglyceride, regeneration of carboxylate salt.

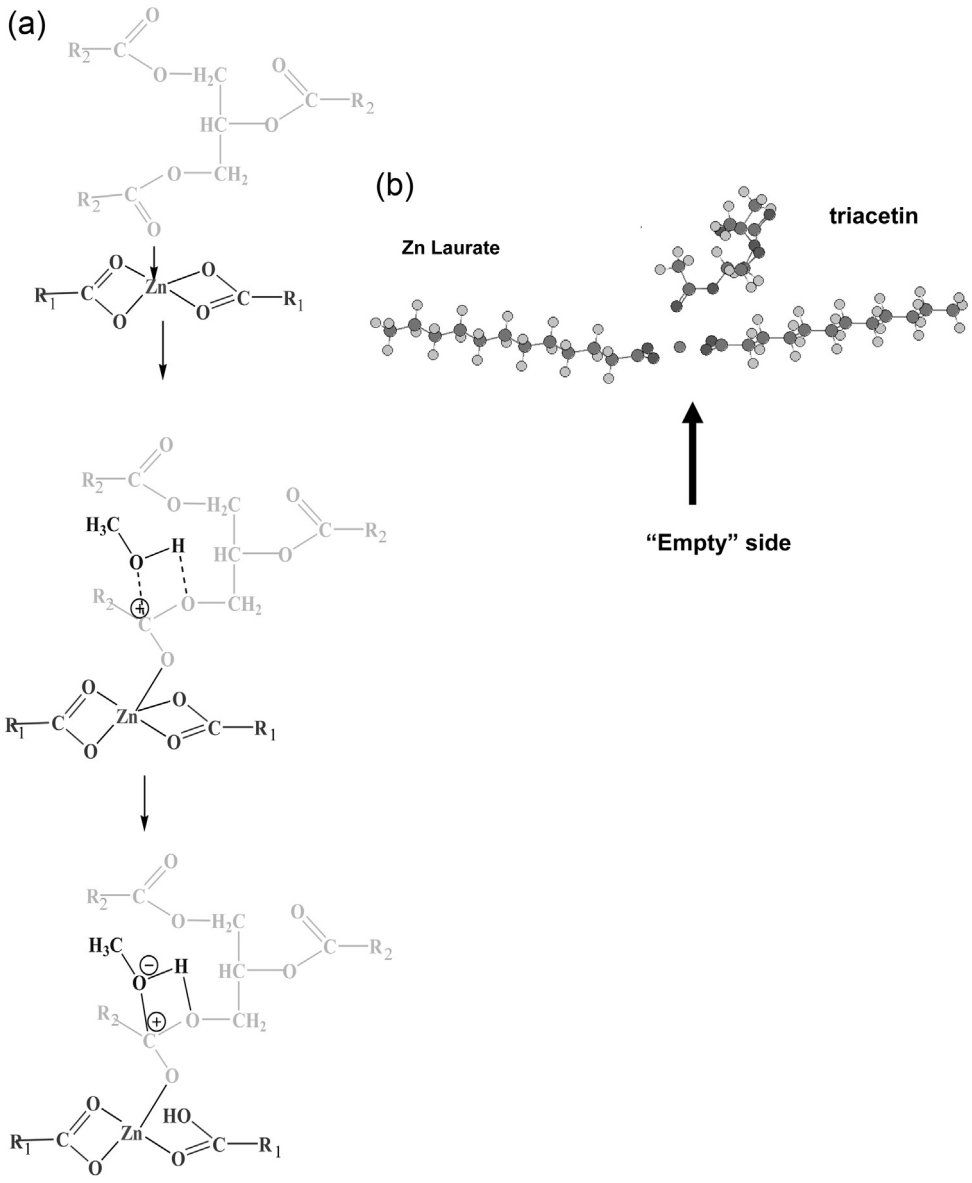

Fig. 3. Mechanism 1: coordination of substrates and intermediates.

Mechanism 3: the co-coordination of methanol and the triglyceride with no carboxylate shift, and the interaction with the triglyceride by H-bonding (Fig. 5).

For Mechanism 3 the following steps were considered:

Step 1: coordination of methanol and triacetin with ZnLa.
Step 2: formation of Zn—OCH_3 bond and carboxylate shift, generation of carboxylic acid coordinated with Zn^{2+}.
Step 3: polarization of C=O of triacetin and reaction.
Step 4: generation of methyl acetate and diglyceride, regeneration of carboxylate salt.

The main steps of the three mechanisms are presented in Figs. 3–5. Step 1 of each mechanism involves different interactions of zinc with substrates:

- Mechanism 1: only triacetin is coordinated and methanol is spectator.
- Mechanism 2: only methanol is coordinated and triacetin is spectator.
- Mechanism 3: both methanol and triacetin are coordinated.

This first step sets the energy of the following ones. The carboxylate shift is assumed to occur in Mechanisms 2 and 3.

Several aspects must be analyzed first. The hydroxyl O of the methanol is highly nucleophilic compared to the O in the carbonyl group of the triglyceride. The carboxylate moieties of the zinc salt may be present with different structures. The enolate form of the carboxylic group could also contribute in the chemical attack as a synergic mechanism of TG coordination [25]. However, as a first step, we focused on the three mechanisms presented above.

Given both the high relative concentration of methanol with respect to triglyceride and the steric and electronic differences favoring methanol, we do not consider that the triglyceride would be coordinated first. If the Zn^{2+} has available methanol, it is first going to coordinate with methanol instead of the carbonyl group of the triglyceride. This coordination can have two different consequences: (A) the carboxylate shift produces a carboxylic acid coordinated as a bidentade ligand, and (B) the

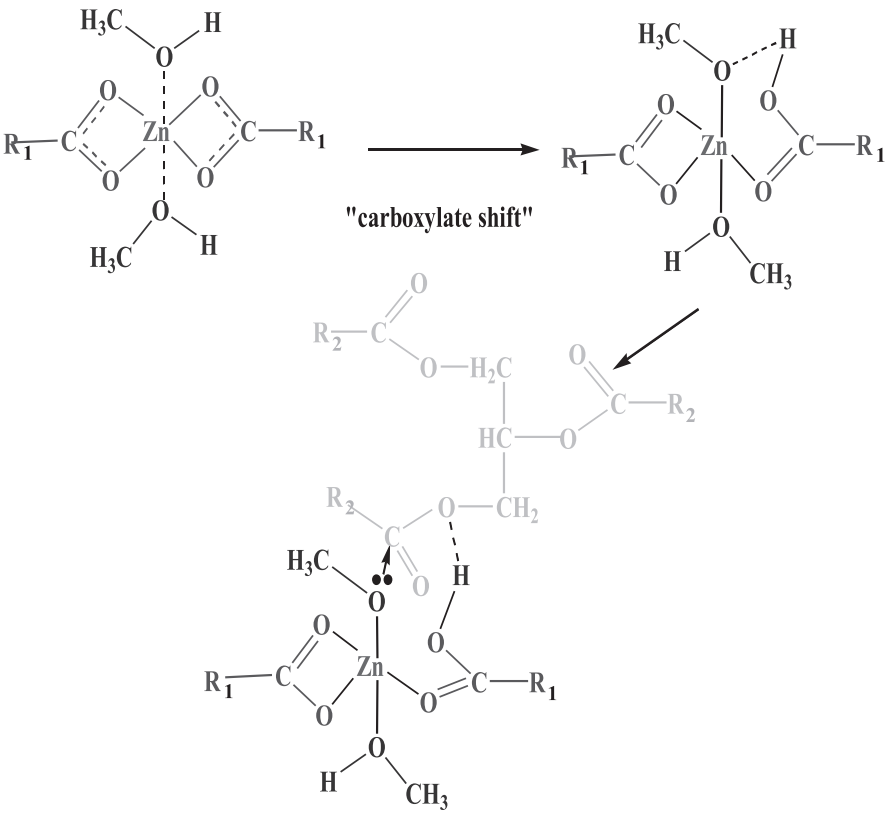

Fig. 4. Mechanism 2: carboxylate shift, alkoxide formation and coordination of triacetin onto methoxide.

triglyceride and the methanol are coordinated by the same side of the carboxylate salt in such a way that no alkoxide is formed and no carboxylate shift occurs.

When methanol is coordinated to the zinc with the displacement of water molecules in the case of zinc acetate dihydrate or zinc laurate, the coordination number of the zinc is 5. The carboxylate shift changes the coordination status of one of the carboxylate groups of the salt (generating the coordinated acid), and therefore the coordination is 5 if the triglyceride is not co-adsorbed to the zinc (Fig. 4). The initial state is octahedral for zinc and later switches between coordination 5 and 6, but never only 4 in the presence of Lewis bases such as those with hydroxyl or carbonyl groups.

3.3. Esterification reaction

The esterification reaction was analyzed within the same framework as the transesterification reaction.

Three esterification mechanisms were studied:

Mechanism 1: only oleic acid is coordinated with ZnLa, and methanol is spectator.
Mechanism 2: only methanol is coordinated with ZnLa, and oleic acid is spectator.
Mechanism 3: both methanol and oleic acid are coordinated with ZnLa.

The steps considered for Mechanism 1 are the following:

Step 1: coordination of fatty acid with ZnLa through the carbonyl group.
Step 2: polarization of the C=O of the fatty acid.
Step 3: interaction of methanol with the polarized C—O of the fatty acid.
Step 4: generation of water and methyl ester of the fatty acid.

For Mechanism 2, the steps are:

Step 1: coordination of methanol with ZnLa.
Step 2: formation of Zn—OCH_3 bond, carboxylate shift, and generation of carboxylic acid coordinated with Zn^{2+}.
Step 3: polarization of C=O of the fatty acid adsorbed onto methoxide.
Step 4: generation of water and fatty acid methyl ester, and regeneration of carboxylate salt.

For Mechanism 3, the following steps were considered:

Step 1: coordination of methanol and fatty acid with ZnLa.
Step 2: formation of Zn—OCH_3 bond, carboxylate shift, and generation of carboxylic acid coordinated to Zn^{2+}.
Step 3: polarization of C=O of the fatty acid and reaction.
Step 4: generation of water and fatty acid methyl ester, and regeneration of carboxylate salt.

The exchange of the carboxylate anion for the fatty acid to be esterified with carboxylate salts was also analyzed. The exchange mechanism occurs through the carboxylate shift (Fig. 2).

4. Results and discussion

4.1. Experimental

4.1.1. Transesterification

Table 3 presents the FAME yields and the triglyceride conversion for the transesterification of soybean oil at 100 °C for 2 h, reported in a previous work [2].

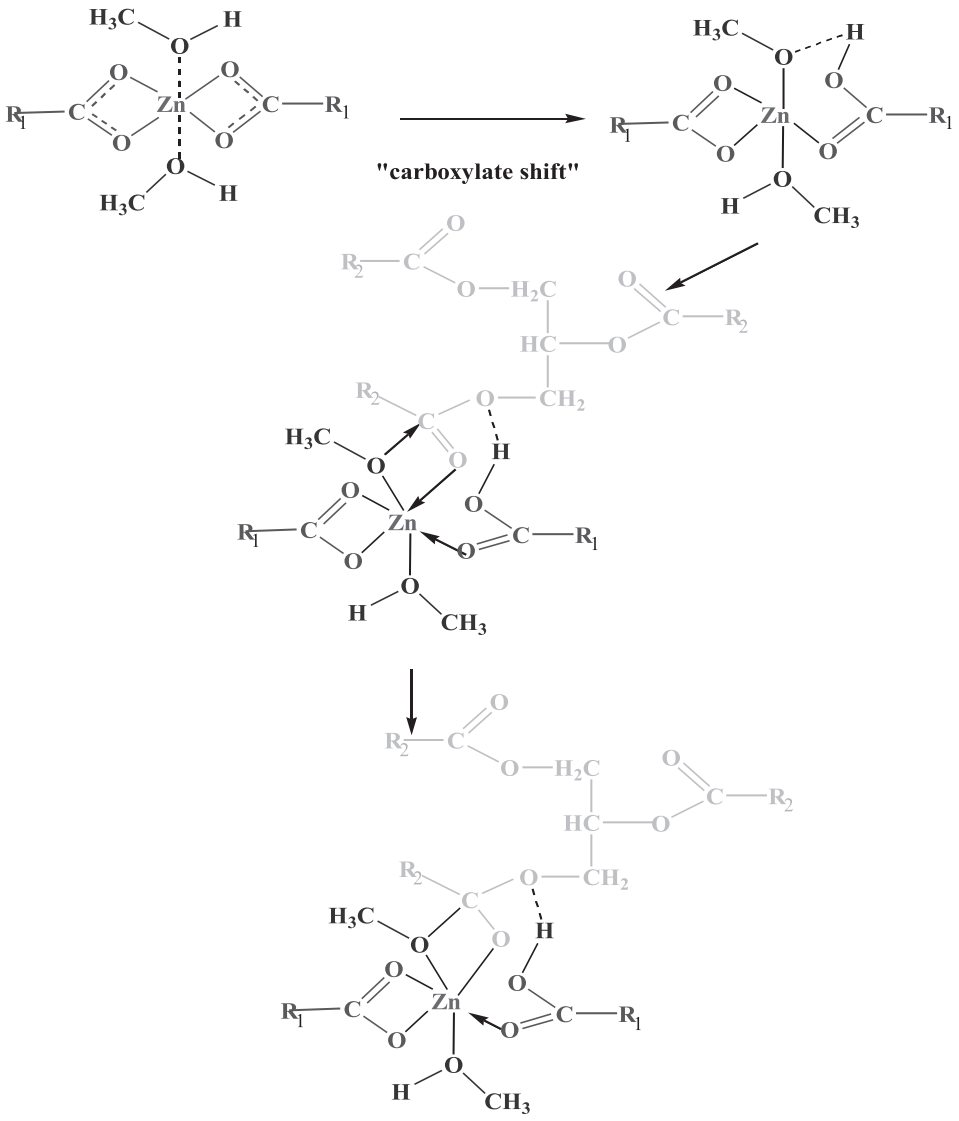

Fig. 5. Mechanism 3: carboxylate shift, alkoxide formation and co-coordination of triacetin.

It can be observed that ZnLa, ZnPa and ZnSt produced oil conversions between 90 and 94% with FAME yields between 68 and 74%. The data obtained by XRD and IR indicated that the solids remained unaltered after three reaction cycles. The ZnAc catalyst presented conversion and yield values similar to those of the solids described above, although it was not stable under the reaction conditions, and it transformed into zinc glycerolate (confirmed using FTIR and XRD, results not shown).

The turn-over frequencies (TOF) calculated from the initial rates are shown in Table 3. For ZnSt, ZnLa, and ZnPa these initial rates were attributed to a similar Lewis acidity of Zn^{2+} and the similar solubility of the salt anions in the non-polar phase of the reaction medium. FAME yields for ZnAc and the rest of the salts were similar, but the TOF values were different. This observation was explained by considering that ZnAc is transformed into zinc glycerolate (ZnGly) during the catalytic test. Under the reaction conditions, Zn carboxylates dissolved, and ZnGly remained solid. The oil:Zn salt ratio in the reactor was higher for ZnAc than for the other studied carboxylates (always 3 wt.%). Therefore, even though ZnGly showed to be less active, it was present in a higher concentration under the reaction conditions than the stable zinc carboxylates, thus originating similar FAME yields.

Table 3
Transesterification of soybean oil with methanol at 100 °C: triglyceride conversion (%), FAME yield (%) and TOF calculated from the initial rates [2].

Reaction time	120 min		TOF (s^{-1})
Catalyst	% conversion	FAME yield	
ZnAc	93.2	74.1	0.021
ZnLa	92.7	70.7	0.042
ZnPa	90.5	68.3	0.053
ZnSt	94.2	67.9	0.045

When the transesterification was studied at 140 °C, it was found that ZnAc and ZnLa transformed completely into zinc glycerolate. On the other hand, for ZnPa and ZnSt (samples with longer saturated fatty acid chains) the transformation to ZnGly was not complete.

The product distribution when the reaction was performed in the presence of water or high concentration of free fatty acid is shown in Table 4. For comparison, the resulting reaction under the same conditions without water (using methanol HPLC grade) is also presented.

The X-ray diffraction patterns of the catalysts used in reaction are shown in Fig. 6. As reported in a previous work [2], the ZnLa catalyst remained unaltered after the transesterification of pure

Table 4
Transesterification of soybean oil with methanol using ZnLa as catalyst (reaction time: 2 h, temperature: 100 °C): food-grade oil (A), acid oil (B), high water-content oil (C).

Composition of the non-polar phase (wt.%)	Soybean oil		
	A	B	C
Monoglycerides	8.2	4.2	11.2
Diglycerides	8.6	0.4	9.9
Triglycerides	7.8	0	3.4
FAME	75.4	92.9	74.8
Fatty acids	0	2.5	0.7
TG conversion (%)	92.7	100	96.8
FAME yield (%)	70.7	75.7	70.6
Initial content (wt.%)			
Water	0	0	0.5
FFA	1.8×10^{-3}	10	1.8×10^{-3}

soybean oil, and it also showed a good tolerance to water. The basal spacing of the spent catalysts remained equal to that of the original catalyst (~33 Å). The XRD pattern for ZnLa used with acid oil corresponds to the ZnSt sample. It seems that the carboxylate anions of the salts were exchanged for the anions of the acid to be esterified.

4.1.2. Esterification

The esterification of oleic acid with methanol was studied at 140 °C in the presence of synthesized Zn carboxylate salts [2]. The solids showed good catalytic activity, with final oleic acid conversions above 60%.

The solids recovered after the reaction (and thoroughly washed) were analyzed by DRX and IR, and it was found that the carboxylate anions of the salts were exchanged for the anions of the acid to be esterified, generating zinc oleate (ZnOl). In the case of ZnAc, the XRD also showed characteristic peaks of zinc oxide. Therefore, this solid is not thermally stable in the reaction medium.

4.1.3. Carboxylate group exchange in the carboxylate salts

The behavior of the Zn salts in the presence of carboxylic acids with different carbon chain lengths was studied according to Table 2, at 20, 60 and 100 °C. The solids recovered after the experiments were analyzed by DRX, and the resulting diffractograms are shown in Fig. 7.

The pattern in Fig. 7a presents the characteristic peak of ZnOl (2θ = 2.2, 6.3 and 4.2°), which resulted from the ZnLa/oleic acid mixture (20 °C). The typical peak for ZnLa is also present (2θ = 3.0, 9.0 and 6.0°), but it completely disappears at 60 °C.

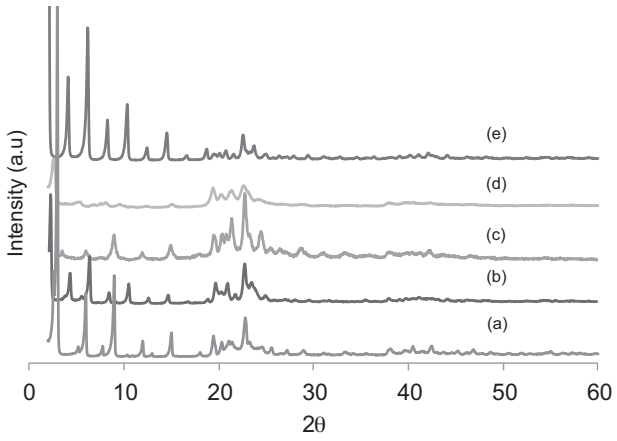

Fig. 6. X-ray diffraction pattern of the (a) ZnLa sample, (b) ZnSt sample, (c) ZnLa after reaction with soybean oil, (d) ZnLa after reaction with soybean oil + 0.5% water and (e) ZnLa after reaction with soybean oil + 10% FFA.

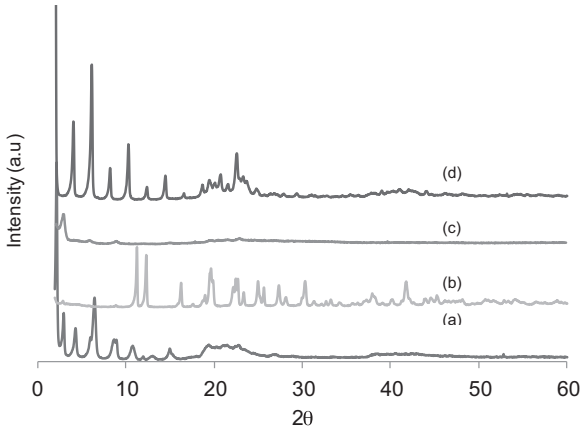

Fig. 7. Study of the behavior of the Zn salts in the presence of carboxylic acids with different carbon chain lengths. XRD of the resulting salts for (a) ZnLa/oleic acid (20 °C), (b) ZnLa/acetic acid (20 °C), (c) ZnOl/lauric acid (20 °C), and (d) ZnS/oleic acid (60 °C).

Fig. 7b shows the XRD of anhydrous ZnAc (with the characteristic peak at 2θ = 11.3, 25.7 and 30.4°) and ZnAc dihydrate (2θ = 12.4, 25.1 and 27.5°), which were formed in the ZnLa/acetic acid mixture (20 °C).

Fig. 7c presents the main peak of ZnLa (2θ = 2.9, 9.1 and 6.1°), formed in the ZnOl/lauric acid mixture (20 °C). Fig. 7d shows the characteristic XRD of ZnOl (2θ = 2.1, 6.3 and 4.2°) for the ZnS/oleic acid mixture (60 °C).

Based on the XRD results, the following conclusions can be summarized:

- For the catalyst with a medium-chain carboxylic anion (ZnLa) in the presence of a long-chain carboxylic acid (oleic acid), and in the case of the catalyst with a long-chain carboxylic anion (ZnOl) in the presence of a short- and medium-chain carboxylic acid (acetic and lauric acid, respectively), the anion exchanges were observed at 20 °C.
- For the Zn salt with a long-chain carboxylic anion (ZnSt) in the presence of a carboxylic acid with the same chain (oleic acid), the anion exchange was observed at 60 °C.

4.2. Theoretical

4.2.1. Transesterification reaction

The basic model for the transesterification reaction includes zinc laurate (ZnLa), 2 methanol molecules (MOH) and 2 triacetin (TAC) molecules. The calculation results for all the steps of the postulated mechanisms are presented in Tables 5–8.

The results of the first step (coordination of substrates onto ZnLa) for the three mechanisms are shown in Table 5. Two different enthalpies are reported: one was obtained by MM2 minimization and the calculation of ΔH_f at that minimum, and the other one was obtained by minimization of the structure using the semi-empiric method PM3. The main goal of using these semi-empirical methods is to obtain qualitative differences. The selected enthalpy used to compare the mechanisms was that obtained for the minimized conformation using PM3. This selection is based on the importance of charge distribution in the steps of the mechanisms.

The combined coordination of methanol and triacetin with the Zn of ZnLa is more stable by 18 kcal/mol in steric energy than the selective coordination of triacetin. The coordination of methanol is favored compared to Mechanism 1 and 3. It is clear that the less sterically hindered structure is the situation presented by Mechanism 3. Thermodynamically, ΔH_f has the most negative value for

Table 5
Adsorption of methanol and/or triacetin on ZnLa (first step of the proposed mechanisms): optimized distances, steric energy and enthalpies of formation of each optimized conformation.

Mechanism	Zn—C1[a] (Å)	Zn—C2[a] (Å)	Zn—O[b] (Å)	Zn—O[c] (Å)	Zn—O[d] (Å)	Zn—O[e] (Å)	Steric energy (kcal/mol)	ΔH_f[f] (kcal/mol)	ΔH_f[g] (kcal/mol)
1	1.94	1.96	2.30	2.42	6.75	4.19	−330.4	−748.46	−847.75
	1.98	1.96							
2	1.98	1.97	4.47	4.29	2.33	2.34	−340.88	−759.13	−881.91
	1.98	1.97							
3	1.99	1.99	2.31	4.12	2.72	2.45	−348.4	−737.47	−874.97
	1.96	1.99							

[a] C1 and C2: carboxylate 1 and 2 in ZnLa, distances to the 2O of each carboxylate.
[b] Zn—O distance from Zn to O of C=O in TAC-1.
[c] Zn—O distance from Zn to O of C=O in TAC-2.
[d] Zn—O distance from Zn to O of OH in MOH-1.
[e] Zn—O distance from Zn to O of OH in MOH-2.
[f] Enthalpy of formation for the minimum in steric energy.
[g] Enthalpy of formation found by PM3 minimization.

Table 6
Formation of C—O alkoxide from the polarization of the C=O of the triacetin (second step of the proposed mechanisms): optimized distances, steric energy and enthalpy of formation.

Mechanism	Zn—C1[a] (Å)	Zn—C2[a] (Å)	Zn—O[b] (Å)	Zn—O[c] (Å)	Zn—O[d] (Å)	Zn—O[e] (Å)	Steric energy (kcal/mol)	ΔH_f[f] (kcal/mol)	ΔH_f[g] (kcal/mol)
1	1.97	2.01	1.85	2.54	4.98	4.34	−371.2	−693.5	−848.9
	2.02	2.02							
2	2.05	2.04	1.86	4.36	4.10	2.48	−366.2	−710.4	−845.6
	1.99	2.00							
3	1.99	2.09	1.86	4.21	2.51	2.78	−371.2	−697.7	−873.1
	2.03	2.03							

[a] C1 and C2: carboxylate 1 and 2 in ZnLa, distances to the 2O of each carboxylate.
[b] Zn—O distance from Zn to O of C=O in TAC-1.
[c] Zn—O distance from Zn to O of C=O in TAC-2.
[d] Zn—O distance from Zn to O of OH in MOH-1.
[e] Zn—O distance from Zn to O of OH in MOH-2.
[f] Enthalpy of formation for the minimum in steric energy.
[g] Enthalpy of formation found by PM3 minimization.

Table 7
Oxonium formation (third step of the proposed mechanisms): optimized distances, steric energy and enthalpy of formation.

Mechanism	Zn—C1[a] (Å)	Zn—C2[a] (Å)	Zn—O[b] (Å)	Zn—O[c] (Å)	Zn—O[d] (Å)	Zn—O[e] (Å)	Steric energy (kcal/mol)	ΔH_f[f] (kcal/mol)	ΔH_f[g] (kcal/mol)
1	2.02	2.16	1.82	2.66	3.48	4.611	−382.6	−676.6	−866.8
	1.98	1.96							
2	2.03	2.18	1.83	4.39	3.42	2.556	−379.6	−688	−852.7
	1.99	1.93							
3	1.98	1.98	1.82	4.2	3.63	2.53	−377.6	−676	−884.8
	2.02	2.26							

[a] C1 and C2: carboxylate 1 and 2 in ZnLa, distances to the 2O of each carboxylate.
[b] Zn—O distance from Zn to O of C=O in TAC-1.
[c] Zn—O distance from Zn to O of C=O in TAC-2.
[d] Zn—O distance from Zn to O of OH in MOH-1.
[e] Zn—O distance from Zn to O of OH in MOH-2.
[f] Enthalpy of formation for the minimum in steric energy.
[g] Enthalpy of formation found by PM3 minimization.

Table 8
Final coordination of methyl acetate and diglyceride: optimized distances, steric energy and enthalpies of formation.

Mechanism	Zn—O C1[a] (Å)	Zn—O C2[a] (Å)	Zn—O[b] (Å)	Zn—O[c] (Å)	Zn—O[d] (Å)	Zn—O[e] (Å)	Steric energy (kcal/mol)	ΔH_f[f] (kcal/mol)	ΔH_f[g] (kcal/mol)
1	1.99	1.94	2.34	2.41	4.39	4.05	−343.2	−745.7	−888.4
	1.95	1.95							
2	2.00	2.00	2.39	2.4	4.37	2.47	−346.2	−728.8	−886.6
	2.00	1.96							
3	2.1	1.96	2.36	4.42	2.77	2.5	−349.7	−743.6	−888.3
	1.95	1.96							

[a] C1 and C2: carboxylate 1 and 2 in Zn Carboxylate, distances to the 2O of each carboxylate.
[b] Zn—O distance from Zn to O of C=O of methyl acetate.
[c] Zn—O distance from Zn to O of C=O in TAC-2.
[d] Zn—O distance from Zn to O of OH in diacetin.
[e] Zn—O distance from Zn to O of OH in MOH-2.
[f] Enthalpy of formation for the minimum in steric energy.
[g] Enthalpy of formation found by PM3 minimization.

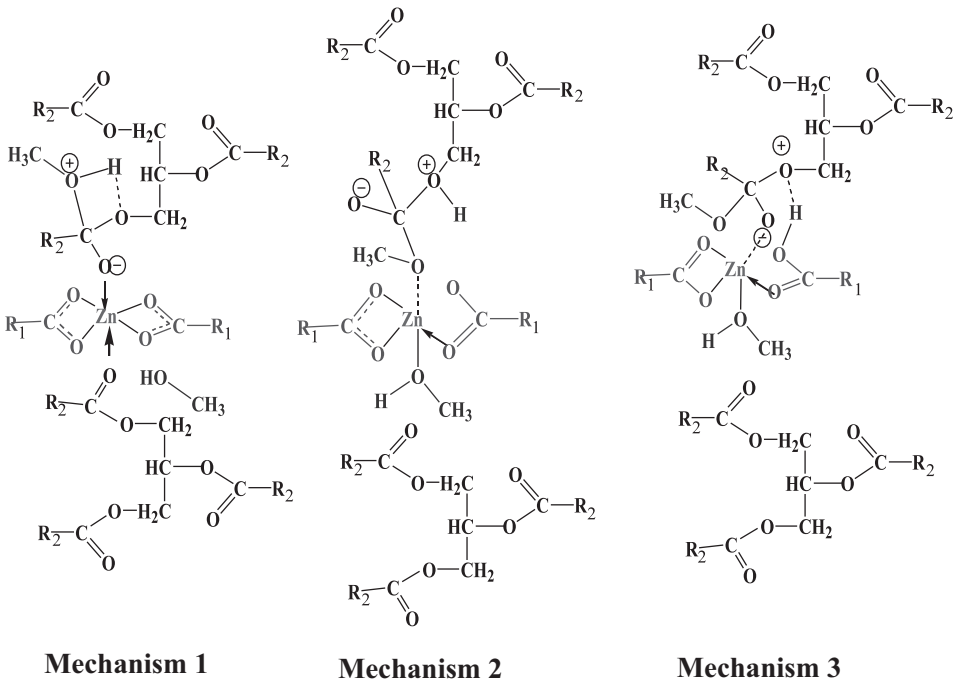

Fig. 8. Oxonium formation (Table 7).

Mechanism 2, obtained by MM2 or PM3 minimization. It seems that methanol coordination as a first step is favored thermodynamically, whereas the co-coordination of the triglyceride implies a barrier close to 10 kcal/mol.

For Mechanisms 2 and 3, the distance from the O of the carboxylate to the H of methanol is 1.98–2.05 Å, and the Zn—O distance in the carboxylate increases by 0.2 or 0.3 Å. These changes are difficult to represent, but it is clear that the H in methanol has a strong

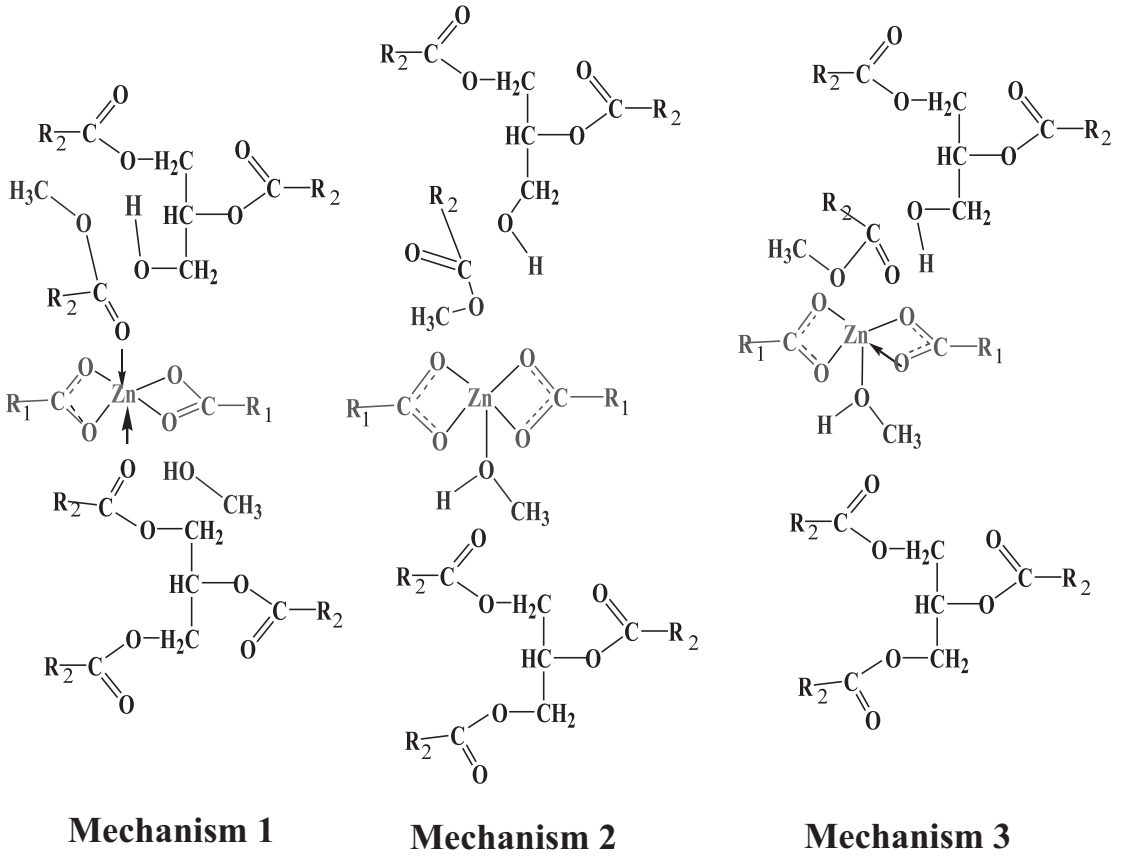

Fig. 9. Final coordination of methyl acetate and diglyceride (Table 8).

interaction with one of the two carboxylates, affecting the charge distribution, in such a way that it is not the type of charge present in a carboxylic acid, neither the charge distribution in a carboxylate anion.

Table 6 shows results for the second step (formation of C—O alkoxide from the polarization of the C=O of the triacetin) of the proposed mechanisms.

For Mechanism 3, the formation of alkoxide through carboxylate shift shows a steric energy of −346.6 kcal/mol and an enthalpy of −726.8 kcal/mol without coordinated substrates.

The different structures found for oxonium formation are shown in Fig. 8, with different special distributions of ligands. Table 7 indicates that the proposed step in Mechanism 3 is energetically favored.

The results of the last step (Fig. 9) for the three mechanisms are shown in Table 8.

The final combined coordination of the diglyceride and the methyl acetate is stabilized by almost 10 kcal/mol compared with the acetate coordination (Fig. 9).

The pathways for the transesterification reaction with ZnLa are shown in Fig. 10. The pathway mechanism named "Combination" is an arrangement of steps from different initial situations (Mechanisms 2 and 3). The latter was the best option, with a barrier of almost 8.8 kcal/mol.

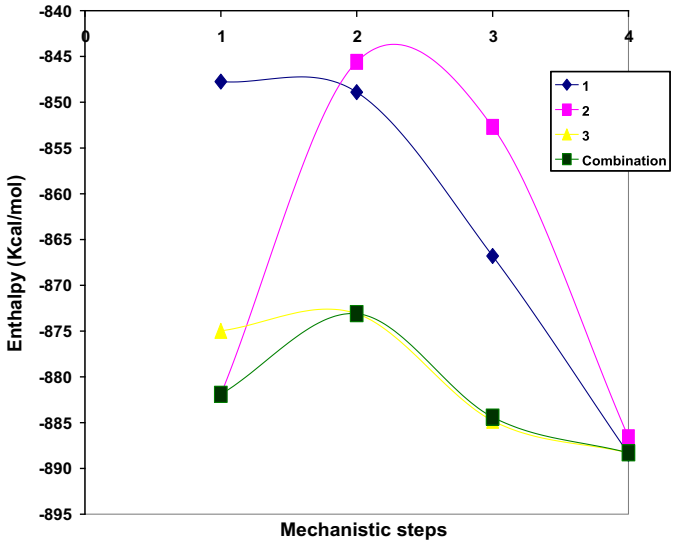

Fig. 10. Reaction pathway for the proposed mechanisms (1, 2, 3 and combination of 2 and 3) for the transesterification of triacetin and methanol as model molecules catalyzed by ZnLa.

4.2.2. Esterification reaction

The basic model for the esterification reaction includes zinc laurate (ZnLa) as catalyst, 2 oleic acid molecules and 2 methanol molecules (MOH).

As mentioned above, three mechanisms were studied. The first step for all the mechanisms is the adsorption/coordination of methanol and a fatty acid with ZnLa. The calculation results for this step are presented in Table 9.

Mechanism 3 was the most favored, with the coordination of methanol and fatty acid with ZnLa.

The reaction steps (Section 4.3) for Mechanism 3 for the esterification reaction are shown in Table 10.

The thermodynamic change for the esterification reaction is endothermic and approximately + 30 kcal/mol. The enthalpic

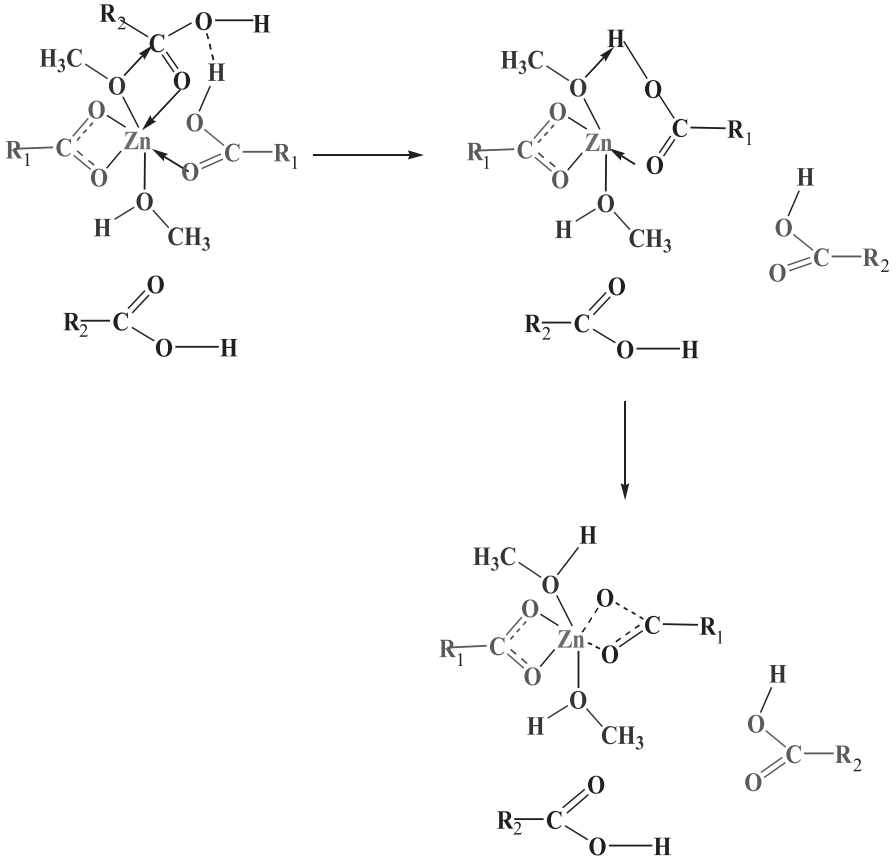

Fig. 11. Exchange of anions in the zinc homogeneous compound in the reaction medium due to the carboxylate shift.

Table 9
Coordination of methanol (MOH) and oleic acid in the esterification reaction for the three proposed mechanisms: optimized distances, steric energy and enthalpies of formation.

Mechanism	Zn—O C1[a] (Å)	Zn—O C2 [a] (Å)	Zn—O[b] (Å)	Zn—O[c] (Å)	Zn—O[d] (Å)	Zn—O[e] (Å)	Steric energy (Å)	ΔH_f [f] (kcal/mol)	ΔH_f [g] (kcal/mol)
1	1.96	1.97	2.384	2.41	5.345	5.134	−362.6	−576.1	No convergence
	1.97	1.97							
2	2.01	2.05	2.35	4.39	2.38	2.57	−379.2	−601.2	−688
	1.96	1.97							
3	1.986	1.997	2.589	2.456	2.513	4.07	−381.9	−560.8	−697
	1.958	1.982							

[a] C1 and C2: carboxylate 1 and 2 in Zn carboxylate, distances to the 2O of each carboxylate.
[b] Zn—O distance from Zn to O of C=O of oleic acid 1.
[c] Zn—O distance from Zn to O of C=O of oleic acid 2.
[d] Zn—O distance from Zn to O of O from CH_3-O in MOH-1.
[e] Zn—O distance from Zn to O of OH (MOH-2).
[f] Enthalpy of formation for the minimum in steric energy.
[g] Enthalpy of formation found by PM3 minimization.

Table 10
Reaction steps for Mechanism 3: optimized distances, steric energy and enthalpies of formation.

Reaction step	Zn—O[a] C1 (Å)	Zn—O[a] C2 (Å)	Zn—O[b] (Å)	Zn—O[c] (Å)	Zn—O[d] (Å)	Zn—O[e] (Å)	Steric energy (kcal/mol)	ΔH_f [f] (kcal/mol)
Formation of alkoxide	1.98	4.21	2.29	2.35	1.74	2.48	−385.2	[g]
	2.04	2.93						
Polarization C=O	2.17	3.91	1.83	2.42	1.76	2.69	−409.5	−678.1[g]
	2.02	2.85						
Tetrahedral intermediary	1.98	3.63	1.76	2.38	3.53	2.41	−373.3	−658.9[g]
	2.00	4.24						
Ester	1.97	1.97	2.98	2.44	2.92	2.42	−366.8	−662.4[g]
	1.98	2.02						

[a] Distances from O of carboxylate to Zn, one of the carboxylates is present as a coordinated carboxylic acid, except at the ester coordination step.
[b] Zn—O distance from Zn to O of C=O of oleic acid 1.
[c] Zn—O distance from Zn to O of C=O of oleic acid 2.
[d] Zn—O distance from Zn to O of O from CH_3-O in MOH-1 (as alkoxide or methanol).
[e] Zn—O distance from Zn to O of OH (MOH-2).
[f] Enthalpy of formation found by PM3 minimization.
[g] Difficult to obtain convergence.

barrier is almost 40 kcal/mol. The anion exchange between the carboxylate of the Zn salt and the fatty acid anion can be associated with the carboxylate shift reaction (Fig. 11).

4.2.3. Carboxylate group exchange in the carboxylate salts

The model includes 2 zinc acetate (ZnAc) and 2 lauric acid molecules. The hydrogen from the lauric acid is transferred to one acetate group in ZnAc.

Fig. 12 presents the enthalpy change when a hydrogen atom is transferred from one lauric acid molecule to one acetate anion of ZnAc. The energy barrier to the hydrogen transfer was approximately 30 kcal/mol.

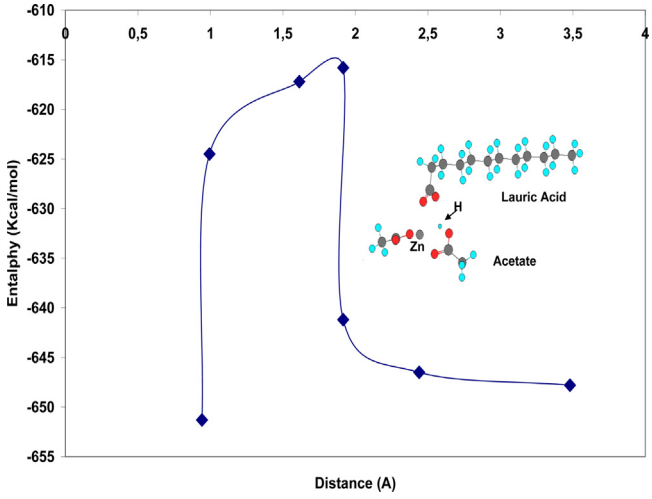

Fig. 12. Hydrogen transfer from one lauric acid to one acetate of ZnAc. Distance from the hydrogen in OH (lauric acid) to the O in the acetate group.

The formation of ZnLa from the reaction of ZnAc with lauric acid in two steps was always exothermic, with a total change in ΔH of −5.2 kcal/mol. In the case of ZnLa exchange with oleic acid, the model included 2 oleic acid molecules and one ZnLa. The total enthalpy change was 0. From the calculation point of view, the exchanges of Ol for La (considering the reaction of ZnOl with lauric acid) and vice versa (considering the reaction of ZnLa with oleic acid) were both equally favored, whereas in the case of the exchange of acetate for a laurate anion the thermodynamics was slightly exothermic, being the exchange of laurate for acetate slightly endothermic.

4.3. Discussion

Considering the results presented and discussed above, several answers can be offered to the original questions presented in the introduction.

The preferred mechanism for the transesterification of triglycerides by methanol includes the initial coordination of methanol, carboxylate shift and the co-coordination of the triglyceride with an alkoxide-like moiety. The classic Lewis acid mechanism proposed in the literature is incomplete. The mechanism presented here has support from the known enzymatic and biomimetic catalysis with zinc containing enzymes. The combined coordination of methanol and triacetin with the zinc of the ZnLa model is more stable by almost 18 kcal/mol in steric energy than the selective coordination of triacetin. Qualitatively, this difference is significant. The preferred mechanism is a combination of steps from different initial situations (Mechanisms 2 and 3 (see Fig. 10)).

The coordination geometry of zinc seems to switch, with a coordination of 6 initially and of 5 during the reaction. This is in agreement with the known coordination of zinc in enzymatic and biomimetic catalysis [26]. This transesterification reaction has a low activation energy calculated from the simple molecular modeling proposed in the present work (10 kcal/mol in the Combination mechanism). This activation energy is consistent with previously reported experimental values [27,28]. The molecular modeling explains and is in line with the high conversions found in the transesterification reactions with zinc carboxylates.

When the esterification reaction is analyzed, the molecular modeling is in agreement with the experimental results: the activation energy for esterification is 4 times the activation energy for transesterification. Therefore, the lower activity of the carboxylate salts in esterification vs. transesterification is easy to understand.

Based on the experimental results of the esterification reaction and the analysis of the molecular modeling, it was observed that the exchange of ligands in the zinc compound is easy and thermodynamically favorable. The length of the carboxylate groups in the salt and in the reaction medium (as available free fatty acid) plays a role that it is not completely understood. All the same, it is important and useful to take these studies into account in order to understand the results obtained in the transesterification of acid oil.

The standard enthalpic change for the exchange of La (medium chain) for Ol (long chain) is 0 by simulation, and experimentally it was observed even at 20 °C. When the exchange is done using fatty acids of the same chain length and different unsaturations (St/Ol), higher temperatures are needed, but the enthalpic change by molecular simulation is 0. This finding implies a kinetic barrier, and probably a role of steric hindrance. The exchange in the case of ZnLa for acetic acid takes place at low temperatures, such as the exchange of lauric for oleate acid and vice versa. Experimentally, it seems that there are further aspects other than thermodynamics affecting these reactions.

Thermodynamic and kinetic aspects, steric hindrance, length and character of the carboxylate moieties in the salt and in the fatty acids, zinc glycerolate and zinc oxide formation and the carboxylate shift reaction have to be considered in order to explain the experimental findings.

5. Conclusions

In this theoretical and experimental study, the mechanisms for the transesterification of triglycerides catalyzed by zinc carboxylates were analyzed and discussed. Different reaction pathways were studied: (A) the classic Lewis acid mechanism with the coordination of the triglyceride through the carbonyl group to the Zn^{2+} ion, (B) the coordination of methanol with the Zn^{2+}, and through the carboxylate shift, the exchange of one of the carboxylate moieties (linked to Zn^{2+} by ionic charges) for the carboxylic acid (bonded to Zn^{2+} by Van der Waals forces through the O of the C=O), and (C) the co-coordination of methanol and the triglyceride with Zn^{2+}, with no carboxylate shift taking place, and the interaction with the triglyceride by H-bonding.

The preferred mechanism included the initial coordination of methanol, carboxylate shift and the co-coordination of the triglyceride with an alkoxide-like moiety.

Fatty acid esterification reaction catalyzed by zinc carboxylates was also studied. The exchange of the carboxylate anion for the fatty acid to be esterified in the Zn salt was presented and analyzed.

The most favored mechanism for the esterification reaction consisted of: (A) coordination of methanol and fatty acid with ZnLa, (B) formation of $Zn—OCH_3$ bond, carboxylate shift, and generation of carboxylic acid coordinated to Zn^{2+}, (C) polarization of the C=O of the fatty acid and reaction, and (d) generation of water and fatty acid methyl ester, and regeneration of carboxylate salt.

The anion exchange between the carboxylate of the Zn salt and the fatty acid can be associated with the carboxylate shift.

It was also shown that it is possible to obtain useful information about the reactions of interest by simple (but well-designed) molecular mechanic simulations and semi-empirical methods, and these findings can be correlated with experimental results.

Acknowledgements

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