

1-*n*-Butyl-3-methylimidazolium tetrachloro-indate (BMI·InCl₄) as a media for the synthesis of biodiesel from vegetable oils

Brenno Amaro DaSilveira Neto^{a,*}, Melquizedeque B. Alves^b, Alexandre A.M. Lapis^c, Fabiane M. Nachtigall^d, Marcos N. Eberlin^d, Jairton Dupont^c, Paulo A.Z. Suarez^{b,*}

^a Centro de Pesquisas em Biologia Molecular e Funcional, Tecnopuc, PUCRS

^b IQ-UnB, CP 4478, CEP 70919-970, DF, Brazil

^c IQ-UFRGS, CP 15003, CEP 91501-970, Porto Alegre, RS, Brazil

^d ThoMSon Mass Spectrometry Laboratory, Institute of Chemistry, State University of Campinas, CP 6154, CEP 13084-862, Campinas, SP, Brazil

Received 23 February 2007; revised 19 April 2007; accepted 20 April 2007

Available online 1 June 2007

Abstract

The complex [Sn(3-hydroxy-2-methyl-4-pyrone)₂(H₂O)₂] immobilized in 1-*n*-butyl-3-methylimidazolium tetrachloro-indate (BMI·InCl₄) ionic liquid forms an effective biphasic catalytic system for the production of biodiesel from the alcoholysis of soybean oil. ESI-MS experiments during the transesterification reaction indicate that the reaction may proceed through the formation of a cationic species formed through the substitution of one pyrone ligand by one alcohol molecule, followed by coordination of the carboxylate compound to tin. The adduct thus formed undergoes transesterification with liberation of the catalytic active species.

© 2007 Elsevier Inc. All rights reserved.

Keywords: Biodiesel; Biofuels; Ionic liquids; Transesterification; Tin catalyst; Vegetable oils; Electrospray ionization mass spectrometry; Ionic liquids

1. Introduction

Imperative concerns related to energy, security, and climate change require the large-scale substitution of petroleum-based fuels [1]. Due to their similarity with petroleum-based fuel, biofuels obtained from triglycerides, such as diesel-like hydrocarbons obtained by thermocatalytic cracking [2] or the biodiesel (mono-alcohol fatty acid esters) produced by alcoholysis, have become very attractive alternatives for diesel engines [3,4]. Of the various protocols for the synthesis of biodiesel [5–9], the methanolysis of vegetable oils catalyzed by metal hydroxides (or alkoxides) and sulfuric acid are the most widely used [10]. Indeed, methyl ester biodiesel has been used since 1988 in European countries as a commercial alternative to the use of fuel [11]. Nevertheless, technological problems, such as cor-

rosion and emulsification, are usually associated with these acid/base methodologies [12,13]. To minimize these problems, several alternative reactants are currently under investigation; such as heterogeneous catalysts, enzymes, and organic bases [5–9]. In this respect, some of us recently showed that metal compounds (e.g., Sn, Pb, Zn) are active catalyst precursors for vegetable oil transesterification under homogeneous conditions, and that the Sn and Zn complexes are more active than the traditional alkaline or acidic catalysts under comparable conditions [14,15]. However, as long as these catalytic systems remain dissolved in the reaction medium, it is difficult to recover and reuse them. One possible solution to solving the drawbacks associated with product separation and catalyst recycling is to use biphasic catalytic systems that immobilize the metal complexes in ionic liquids (ILs) [16,17]. These biphasic systems in ILs combine the advantages of both homogeneous (greater catalyst efficiency and mild reaction conditions) and heterogeneous (ease of catalyst recycling and separation of products) catalysis [18,19]. However, our first attempts to develop a biphasic catalytic system suitable for recovering

* Corresponding authors. Fax: +55 61 273 4149.

E-mail addresses: brenno.silveira@pucrs.br, brenno.ipi@gmail.com (B.A. DaSilveira Neto), dupont@iq.ufrgs.br (J. Dupont), psuarez@unb.br (P.A.Z. Suarez).

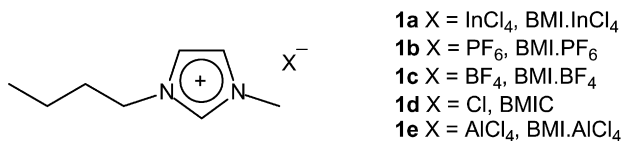


Fig. 1. Some imidazolium-based IL commonly used in catalysis.

and reuse by anchoring the catalyst precursor Sn(3-hydroxy-2-methyl-4-pyrone)₂(H₂O)₂ in classical ionic liquids such as **1b** (Fig. 1) met with little success [20]. The complex dissolved in IL was as active as under homogeneous conditions, but after recovering and reusing the same ionic phase, the reaction yield drastically fell with each new substrate charge, dropping from 58% in the first charge to almost zero in the third one, probably due to extensive leaching of the catalyst from the ionic phase. Nonetheless, it is reasonable to assume that the use of other ILs, particularly those with inherent Lewis acidity, may constitute a more stable and robust catalytic system for the alcoholysis of triglycerides. In this respect, it was recently reported that the IL 1-*n*-butyl-3-methylimidazolium tetrachloroindate (BMI-InCl₄) **1a** (Fig. 1) has Lewis acid character and been successfully used for the tetrahydropyranylation of alcohols [21], hydroamination/hydroarylation reactions [22], and mediated nucleophilic addition of carbon nucleophiles to cyclic *N*-acyliminium ions [23].

Herein we report our main results on the use of BMI-InCl₄ as a medium for multiphase catalysis in biodiesel synthesis from vegetable oils.

2. Methodology

2.1. General

All reagents were obtained from commercial sources and used without further purification. Reagent-grade 3-hydroxy-2-methyl-4-pyrone, acetyl-acetone, aluminum(III) oxide, lanthanide(III) chloride, cerium(III) chloride, barium(II) chloride, titanium(III) chloride, zirconium(IV) chloride, copper(II) bromide, copper(I) iodide, magnesium(II) chloride, zinc(II) chloride, germanium(IV) oxide, cadmium(II) chloride, platinum(IV) chloride, platinum(II) chloride, nickel(II) chloride, tin(II) chloride, indium(III) chloride, Na₂SiF₆, and BF₃·OEt₂ were obtained from Aldrich. Nb₂O₅(H₂O) were obtained from CBMM. Methylimidazole and butylchloride were obtained from Acros. Edible vegetable oils were purchased from commercial sources.

The BMIC **1d** [24] and BMI-InCl₄ **1a** [21] compounds and the Sn(acac)₂ [20], Sn(pyrone)₂(H₂O)₂ [14], Hg(pyrone)₂(H₂O)₂

[14], Pt(pyrone)₂(H₂O)₂ [14], and Ni(pyrone)₂(H₂O)₂ [14] complexes were prepared as described previously.

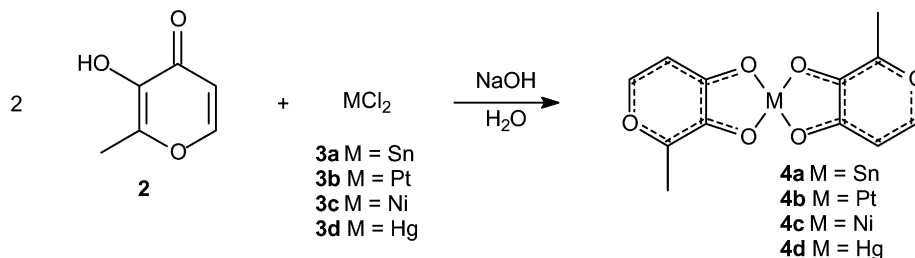
High-performance liquid chromatography (HPLC) was performed using a Shimadzu CTO-20A chromatograph with a UV-vis detector at λ = 205 nm, equipped with a Shim-Pack VP-ODS column (C-18, 250 mm, 4.6 mm i.d.). The solvents were filtered through a 0.45-μm Millipore filter before use. An injection volume of 10 μL and a flow rate of 1 mL/min were used in all experiments. The column temperature was held constant at 40 °C. All samples were dissolved in 2-propanol–hexane (5:4, v/v). A 35-min ternary gradient with two linear gradient steps was using, comprising 30% water and 70% acetonitrile for 0 min, 100% acetonitrile for 10 min, 50% acetonitrile and 50% 2-propanol–hexane (4:5, v:v) for 2 min, and isocratic elution with 50% acetonitrile and 50% 2-propanol–hexane (4:5, v:v) for the last 15 min. Electrospray mass and tandem mass spectra were recorded on a Q-ToF (Micromass) mass spectrometer with a scanning quadrupole (Q), a hexapole collision cell, and a high-resolution orthogonal time-of-flight (*o*-TOF) analyzer. The sample introduction was performed using a syringe pump (Harvard Apparatus, Pump 11) set to 10 μL/min pumped through an uncoated fused-silica capillary. All samples (from reaction) were diluted in acetonitrile or methanol. The ESI-MS were acquired using an ESI capillary voltage of 3 kV and a cone voltage of 10 V. Isotopic patterns were calculated using the MassLynx software.

2.2. Catalytic experiments

The different vegetable oils (10 g) were transesterified in BMI-InCl₄ **1a** (3 mL) in the presence of various catalysts (0.1 g). The reaction mixtures were kept in a 50-mL batch reactor in reflux (approximately 80 °C) and under magnetic stirring for the desired time. The product obtained was separated by decantation. The ionic liquid phase (always lower phase) retains the catalyst and the majority of byproducts. The upper phase was separated, and the product was obtained under almost pure form. The recovered esters were analyzed. Glycerol can be recovered by freezing the ionic phase and removing the IL once glycerol freezes or washing the ionic liquid with water and recover the glycerol in the aqueous phase.

3. Results and discussion

Initially, an exploratory study was carried out using several simple alkaline and acidic catalyst precursors [14] (Scheme 1)



Scheme 1. Synthesis of the catalysts **4a–4d**.

Table 1
Conditions and product yields for methanolysis of soybean oil, with different catalysts, in the IL BMI-InCl₄ **1a**^a

Entry	Catalyst	Fat acids (%) ^c	Monoglyceride (%) ^c	Diglyceride (%) ^c	Triglyceride (%) ^c	Not identified (%) ^c	Biodiesel (%) ^{d,e}
1	–	2	Traces	1	94	1	1
2	InCl ₃	Traces	Traces	1	95	1	2
3 ^b	InCl ₃	Traces	Traces	1	93	1	4
4	Al ₂ O ₃	2	Traces	2	94	1	Traces
5	LaCl ₃	Traces	Traces	1	96	Traces	2
6	CeCl ₃	Traces	Traces	Traces	97	Traces	2
7	BF ₃ ·OEt ₂	1	Traces	3	91	1	3
8	BaCl ₂	1	Traces	2	85	2	9
9	SnCl ₂	1	1	1	94	2	1
10	Sn(Acac) ₂	Traces	1	1	87	1	9
11	Sn(pyrono) ₂ ^c	1	Traces	2	79	1	16
12	TiCl ₃	Traces	1	2	93	2	1
13	ZrCl ₄	1	1	1	94	2	1
14	NiCl ₂	2	1	1	92	2	2
15	CuBr ₂	Traces	Traces	1	96	2	Traces
16	CuI	Traces	Traces	1	97	1	Traces
17	MgCl ₂	Traces	1	3	90	1	4
18	ZnCl ₂	Traces	1	1	91	1	5
19	GeO ₂	Traces	Traces	1	95	1	2
20	PtCl ₄	Traces	Traces	1	98	Traces	Traces
21	CdCl ₂	1	3	1	90	3	2
22	Pt(pyrono) ₂ ^c	2	1	2	92	2	1
23	Ni(pyrono) ₂ ^c	Traces	Traces	1	96	1	1
24	Nb ₂ O ₅ (H ₂ O)	1	1	1	95	Traces	1
25	Sn (0)	Traces	6	1	89	1	2
26	Hg(pyrono) ₂ ^c	Traces	Traces	1	96	2	Traces
27	Na ₂ SiF ₆	Traces	Traces	Traces	99	Traces	Traces
28	PdCl ₂	Traces	Traces	1	98	Traces	Traces

^a 10 g of soybean oil, 3 g of MeOH, 3 mL of BMI-InCl₄ **1a**, 0.100 g of catalyst, reflux, 1 h.

^b 3 h of reaction.

^c Synthesized according to Ref. [15].

^d Biodiesel = methyl ester.

^e Determined by HPLC.

Table 2
Conditions and products from attempts to optimize reaction time for the methanolysis of soybean oil using Sn(pyrono)₂ **4a** in the IL BMI-InCl₄ **1a**^a

Time (h)	Not identified (%) ^c	Fat acids (%) ^c	Monoglyceride (%) ^c	Diglyceride (%) ^c	Triglyceride (%) ^c	Biodiesel (%) ^{b,c}
1	1	1	Traces	2	79	16
2	7	Traces	1	1	42	48
3	4	2	1	Traces	14	78
4	4	Traces	Traces	Traces	12	83
5	7	1	1	1	16	74
6	6	Traces	Traces	1	16	76
7	11	Traces	1	1	39	47
8	14	Traces	1	1	17	66
9	14	1	Traces	1	9	74
10	8	1	Traces	1	5	84

^a 10 g of soybean oil, 3 g of MeOH, 3 mL of BMI-InCl₄ **1a**, 0.100 g of Sn(pyrono)₂ **4a**, reflux.

^b Biodiesel = methyl ester.

^c Determined by HPLC.

in the IL **1a** for the methanolysis of soybean oil under the same reaction conditions. Table 1 summarizes the results.

Without the addition of any catalyst (Table 1, entry 1), no product was observed, indicating that the Lewis acid property inherent of IL **1a** was not strong enough to promote transesterification. The addition of InCl₃ failed to show the expected effect as for the other experiments [21–23] (Table 1, entry 2)

and satisfactory results were not obtained even after 3 h (Table 1, entry 3). The use of lanthanide metals, such as Ce and La, provided virtually no products (Table 1, entries 5 and 6). The use of complexes of transition metals (e.g., Pd, Pt, Zn, Ni) and most of the main elements (Na, Mg, B, Si, Al, and Ge) also failed to promote transesterification. Earth-alkaline metal complexes (e.g., Ba, Mg) were ineffective in furnishing the desired

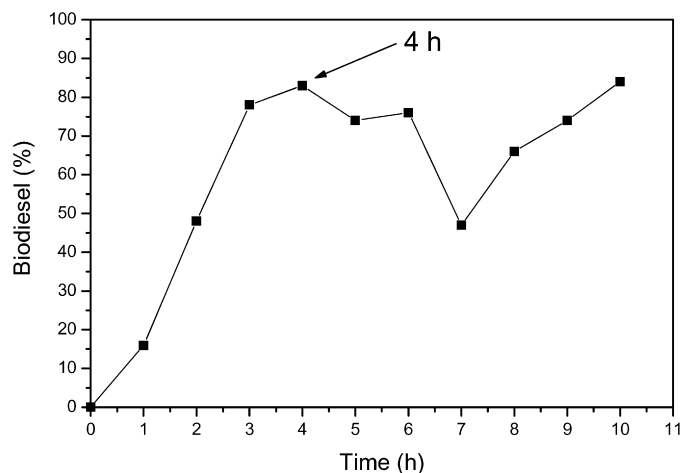


Fig. 2. Optimization of reaction time for the methanolysis of soybean oil in the system Sn(pyronone)₂ **4a** in BMI-InCl₄ **1a**.

product. The best activities were obtained for the earth alkaline Ba (Table 1, entry 8) and acidic tin complexes (Table 1, entries 10 and 11). SnCl₂ was also tested (Table 1, entry 9) but with lower efficiency compared with the respective Sn complexes.

The reaction conditions for the soybean oil methanolysis were optimized using Sn(3-hydroxy-2-methyl-4-pyrone)₂-(H₂O)₂ in IL **1a**. Table 2 and Fig. 2 show the reaction yields

of methyl fatty esters over a period of 10 h. As Fig. 2 shows, the reaction yield reaches a maximum after 4 h (83%), and after this time it decreases to a minimum and later it increases once again. This behavior can be explained by the reversibility of this reaction, where some glycerolysis of the methyl fatty esters probably occurs as already observed using other catalytic systems [14,25,26].

The possibility of catalyst recycling was investigated using the heterogeneous system BMI-InCl₄ **1a** and the tin catalyst **4a** (Table 3) in the methanolysis of soybean oil. From the data on Table 3, we can see that the system is unable to sustain its activity already in the second recharge. In the third recharge, this fact is most pronouncedly for the third recharge of MeOH and soybean oil. The yield of the first reaction remains similar (83%). The tin-based catalysts, both Sn(Acac)₂ and Sn(pyronone)₂ decompose under the reactions conditions, and this observation was further corroborated by the ESI-MS investigation (see below). Using the IL BMI-PF₆ **1b** instead of BMI-InCl₄ **1a** also leads to a two-phase system under the same reaction conditions used for the methanolysis process [20]. However, the reaction yield was 55% for the first charge, 5% in the second, and, as already discussed, nearly zero in the third reaction. This behavior is probably caused by the leaching of the catalyst when the IL **1b** is used. Using the IL **1a**, the system maintained its activity in the second (25%) charge, demonstrating that the organoindate

Table 3

Products and yields obtained during attempts to recycling using the system Sn(pyronone)₂ **4a** in BMI-InCl₄ **1a**^a

Entry	Not identified (%) ^c	Fat acids (%) ^c	Monoglyceride (%) ^c	Diglyceride (%) ^c	Triglyceride (%) ^c	Biodiesel (%) ^{b,c}
1	4	Traces	Traces	Traces	12	83
2 ^d	3	Traces	Traces	11	60	25
3 ^e	4	1	1	3	88	3
4 ^f	Traces	Traces	Traces	Traces	99	Traces
5 ^g	Traces	Traces	Traces	Traces	99	Traces

^a For each reaction: 10 g of soybean oil, 3 g of MeOH at reflux temperature for 4 h. 3 mL of BMI-InCl₄ **1a** and 100 mg of **4a** was employed in the first reaction.

^b Biodiesel = methyl ester.

^c Determined by HPLC.

^d Recharge from 1.

^e Recharge from 2.

^f Recharge from 3.

^g Recharge from 4.

Table 4

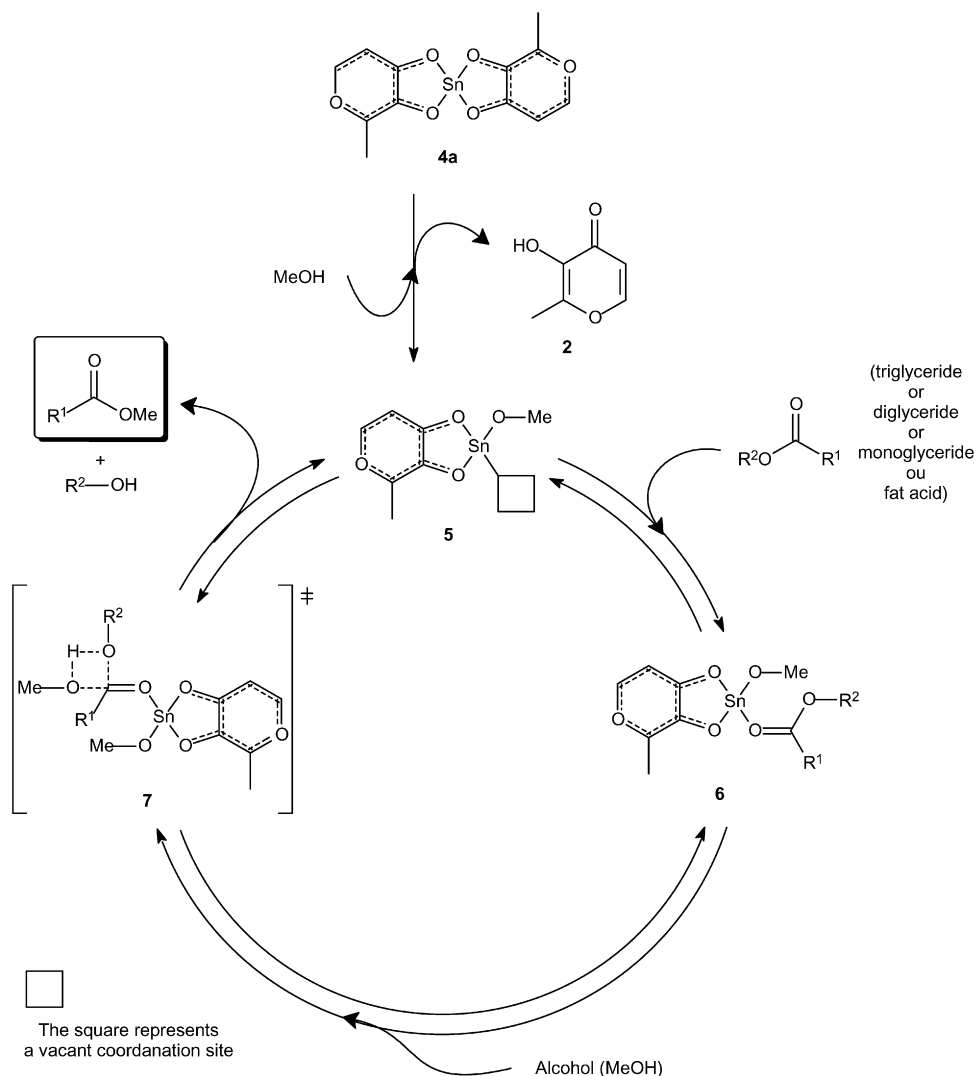
Products and yields for transesterification reactions of different alcohols using the developed catalytic system^a

Alcohol	Not identified (%) ^c	Fat acids (%) ^c	Monoglyceride (%) ^c	Diglyceride (%) ^c	Triglyceride (%) ^c	Transesterification product (%) ^{b,c}
MeOH	4	Traces	Traces	Traces	12	83
EtOH	3	Traces	Traces	1	53	42
<i>n</i> -PrOH	5	2	Traces	10	42	40
<i>n</i> -BuOH	1	1	1	4	78	15
<i>i</i> -PrOH	1	Traces	Traces	2	84	12
<i>t</i> -BuOH	2	1	Traces	2	90	4
Octanol	1	4	5	16	70	4
Cyclohexanol	5	1	2	5	79	8
PhOH	3	2	2	9	42	42
BnOH	Traces	1	2	4	52	40

^a 10 g of soybean oil, 94 mmol of the alcohol at reflux temperature for 4 h. 3 mL of BMI-InCl₄ **1a** and 100 mg of **4a**.

^b New formed ester.

^c Determined by HPLC.



Scheme 2. Proposed catalytic cycle for transesterification.

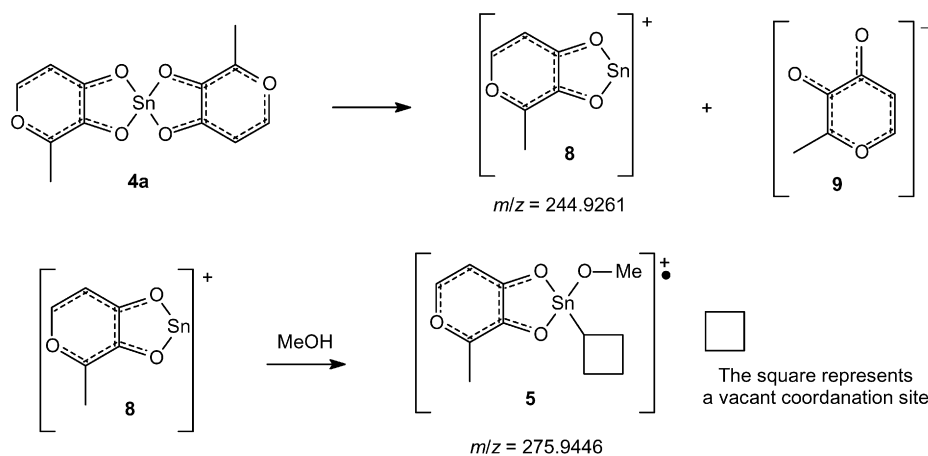


Fig. 3. Charged intermediates of the methanolysis reaction.

IL **1a** is even more effective for the stabilization of the intermediates of catalytic cycle and that this specific IL **1a** is able to keep the tin catalyst in its phase during the separation and recharging process (see further discussions below).

The activity of the developed system to perform transesterification reactions using different alcohols was also tested; the results are presented in Table 4. All reactions were conducted under the conditions optimized for the methanolysis process.

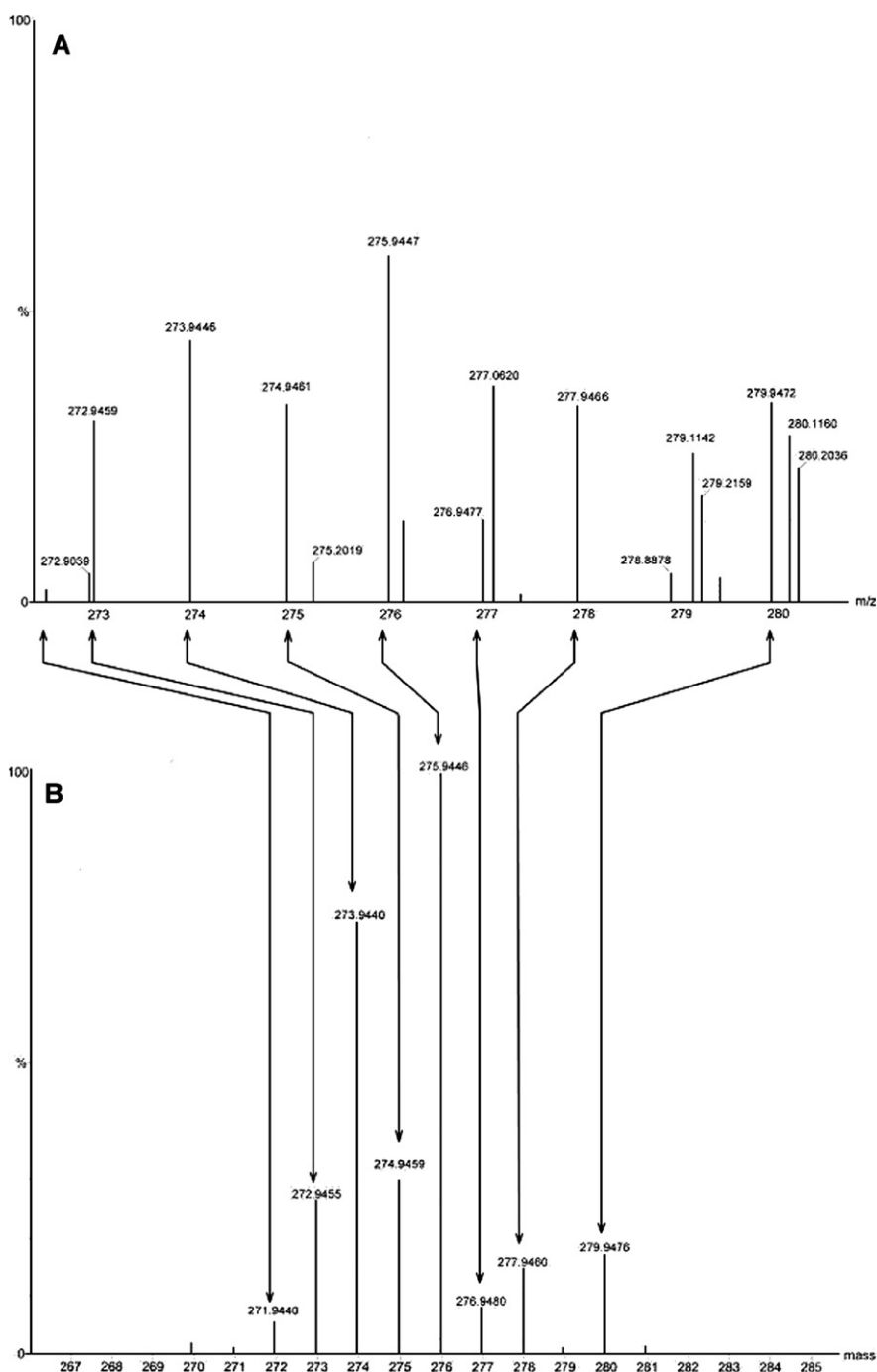


Fig. 4. High resolution detected (A) and simulated (B) ESI(+)-MS of the ion with the $C_7H_8O_4Sn$ composition (**5**).

Table 5

Measured and simulated m/z for intermediate **5** ($C_7H_8O_4Sn^+$)

m/z (measured)	271.9449	272.9459	273.9446	274.9461	275.9447	276.9477	277.9466	279.9472
m/z (simulated)	271.9440	272.9455	273.9440	274.9459	275.9446	276.9480	277.9460	279.9476

Table 4 shows that transesterification occurs in relatively good yield even with no changes in the experimental conditions. Some results are significant, such as that for the transesterification with *i*-PrOH that forms the desired product with 12% yield. Considering that the experimental conditions can be further optimized (time and temperature) for the transesterification using

this alcohol, the present result is very satisfactory. Using BnOH (Bn = benzyl) and PhOH also resulted in the desired transesterification product in good yield (40 and 42%, respectively) under the catalytic conditions. A secondary alcohol (cyclohexanol) and a tertiary alcohol (*t*-BuOH) failed to provide good results, probably due to steric constraints.

To gain insight into the mechanism of the transesterification reaction of soybean oil with methanol promoted with catalyst **4a**, we monitored the reaction by electrospray ionization mass spectrometry [27,28]. Note that ESI-MS and ESI-MS/MS has been shown to be an adequate technique for studying reaction mechanisms via the interception and structural characterization of key ionic intermediates, even when present in reactions performed in the presence of ionic liquids [29,30]. As pointed out previously [15], it is usually assumed that the transesterification probably follows a mechanism (Scheme 2) similar to those proposed for polyesterification reactions catalyzed by divalent metals [31,32]. It is assumed that these catalysts act as a Lewis acid during catalysis.

In the presence of methanol, the catalytically active species **5** is formed, which allows the coordination of the carbonyl-containing compound (triglyceride, diglyceride, monoglyceride, or the fatty acid). This coordination increases the natural polarization of the carbonyl compound, thus facilitating nucleophilic attack by the alcohol. The so-formed species **6** probably develops via a four-center transition state **7** (as proposed previously [31]) that furnishes the desired biodiesel (methyl ester).

To prove that fatty acids also could undergo esterification under the conditions used in catalysis, as we proposed in Scheme 2, we used a pure sample of fatty acid previously hydrolyzed from soybean oil. Because this property had not been exploited before, we decided to investigate it. After 1 h of reaction, the conversion of fatty acids to the corresponding methyl esters was 50% (determined by HPLC), indicating that the biodiesel formation occurs through two different pathways: transesterification and direct esterification of the formed acid. Therefore, we used ESI-MS in an attempt to intercept and characterize the charged intermediates (Fig. 3) of the proposed reaction cycle (Scheme 2).

When using ESI(–)-MS (negative ion mode), no ion directly related to the proposed reaction cycle could be detected. However, when using ESI(+)-MS, interesting intermediates were detected and characterized. In the experiment performed using only acetonitrile as a solvent, ESI(+)-MS detected and ESI(+)-MS/MS characterized intermediate **8** of m/z 244.9261 (data not shown) formed from the decoordination of one pyrone anion **9**. But our main goal was to detect and characterize the intermediate **5**, a cationic species [or a cation-radical species in the ESI(+)-MS process]. Nevertheless, no ion of m/z 275 (intermediate **5**) was detected. When methanol was added (or a solution in pure methanol was used), ESI(+)-MS detected a radical cation of m/z 275.9447, which was characterized as the catalytic active species **5** (Fig. 4). This radical cation likely was formed during the ESI process.

Fig. 4 shows the characteristic set of Sn isotopologue ions with m/z and relative abundance in excellent agreement with those of the simulated spectra (see Table 5). Due to the small amount of the isotopologue ions of **5**, ESI-MS/MS could not be acquired, but the characteristic isotopic pattern and m/z accuracy point firmly to the interception of intermediate **5**.

ESI-MS analysis of the ionic liquid phase and the organic phase before and after catalysis indicates that tin fragments re-

main in the IL phase but shows no sign of the catalyst. Thus, this decomposition is the likely reason for the loss of activity noted in the recycling experiments. The biodiesel phase is almost pure, and simple decantation is sufficient to separate the desired product.

4. Conclusion

The production of biodiesel from soybean oil may be accomplished by using catalysts (particularly the tin catalyst **4a**) in the IL 1-*n*-butyl-3-methylimidazolium tetrachloroindate (BMI·InCl₄) **1a**. Methanolysis, the most important process, occurs in high yields and in short reaction times. ESI-MS screening corroborated the proposed transesterification mechanism by intercepting a key ionic intermediate (**5**; Scheme 2). Based on our previous results reported herein, the development of more stable catalysts to perform biodiesel synthesis in IL can be achieved, and efforts toward this end are currently underway in our laboratories.

Acknowledgments

Financial support was provided by CNPQ, FBB, Finatec, FAPDF, CTPETRO, FAPESP, and CTENERG. P.A.Z.S., J.D., and M.N.E. thank CNPq for a research fellowship. The authors also thank Dr. John Spencer of Greenwich University for a critical reading of the manuscript and helpful suggestions.

References

- [1] A.E. Farrell, R.J. Plevin, B.T. Turner, A.D. Jones, M. O'Hare, D.M. Kammen, *Science* 311 (2006) 506–508.
- [2] D.G. Lima, V.C.D. Soares, E.B. Ribeiro, D.A. Carvalho, E.C.V. Cardoso, F.C. Rassi, K.C. Mundim, J.C. Rubim, P.A.Z. Suarez, *J. Anal. Appl. Pyrolysis* 71 (2004) 987–996.
- [3] E.H. Pryde, *J. Am. Oil Chem. Soc.* 60 (1983) 1557–1558.
- [4] E.G. Shay, *Biomass Bioenergy* 4 (1993) 227.
- [5] F.R. Ma, M.A. Hanna, *Bioresour. Technol.* 70 (1999) 1–15.
- [6] A.C. Pinto, L.L.N. Guarieiro, M.J.C. Rezende, N.M. Ribeiro, E.A. Torres, W.A. Lopes, P.A.D. Pereira, J.B. De Andrade, *J. Braz. Chem. Soc.* 16 (2005) 1313–1330.
- [7] U. Schuchardt, R. Sercheli, R.M. Vargas, *J. Braz. Chem. Soc.* 9 (1998) 199.
- [8] X. Lang, A.K. Dalai, N.N. Bakhshi, M.J. Reaney, P.B. Hertz, *Bioresour. Technol.* 80 (2001) 62.
- [9] H. Fukuda, A. Kondo, H. Noda, *J. Biosci. Bioeng.* 92 (2001) 406.
- [10] S. Bhattacharyya, C.S. Reddy, *J. Agric. Eng. Res.* 54 (1994) 157–166.
- [11] X. Lang, A.K. Dalai, N.N. Bakhshi, M.J. Reaney, P.B. Hertz, *Bioresour. Technol.* 80 (2001) 53–62.
- [12] G. Antolín, F.V. Tinaut, Y. Briceño, V. Castaño, C. Pérez, A.I. Ramírez, *Bioresour. Technol.* 83 (2002) 111–114.
- [13] B. Freedman, E.H. Pryde, T.L. Mounts, *J. Am. Oil Chem. Soc.* 61 (1984) 1638–1643.
- [14] F.R. Abreu, D.G. Lima, E.H. Hamu, S. Einloft, J.C. Rubim, P.A.Z. Suarez, *J. Am. Oil Chem. Soc.* 80 (2003) 601–604.
- [15] F.R. Abreu, D.G. Lima, E.H. Hamu, C.R. Wolf, P.A.Z. Suarez, *J. Mol. Catal. A Chem.* 209 (2004) 29–33.
- [16] J. Dupont, C.S. Consorti, J. Spencer, *J. Braz. Chem. Soc.* 11 (2000) 337–344.
- [17] B.A.D. Neto, L.S. Santos, F.M. Nachtigall, M.N. Eberlin, J. Dupont, *Angew. Chem. Int. Ed.* 118 (2006) 7409–7412.

- [18] J. Dupont, R.F. De Souza, P.A.Z. Suarez, *Chem. Rev.* 102 (2002) 3667–3692.
- [19] Z. Guo, X. Xu, *Green Chem.* 8 (2006) 54–62.
- [20] F.R. Abreu, M.B. Alves, C.C.S. Macêdo, L.F. Zara, P.A.Z. Suarez, *J. Mol. Catal. A Chem.* 227 (2005) 263–267.
- [21] B.A.D. Neto, G. Ebeling, R.S. Gonçalves, F.C. Gozzo, M.N. Eberlin, J. Dupont, *J. Synth.* (2004) 1155–1158.
- [22] A.A.M. Lapis, B.A.D. Neto, J.D. Scholten, F.M. Nachtigall, M.N. Eberlin, J. Dupont, *Tetrahedron Lett.* 47 (2006) 6775–6779.
- [23] R.A. Pilli, L.G. Robello, N.S. Camilo, J. Dupont, A.A.M. Lapis, B.A.D. Neto, *Tetrahedron Lett.* 47 (2006) 1669–1672.
- [24] J. Dupont, C.S. Consorti, P.A.Z. Suarez, R.F. de Souza, *Org. Synth.* 79 (2002) 236.
- [25] M. Di Serio, R. Tesser, M. Dimiccoli, F. Cammarotaa, M. Nastasi, E. Santacesaria, *J. Mol. Catal. A* 239 (2005) 111.
- [26] S.M.P. Meneghetti, M.R. Meneghetti, C.R. Wolf, E.C. Silva, G.E.S. Lima, M.A. Coimbra, J.I. Soletti, S.H.V. Carvalho, *J. Am. Oil Chem. Soc.* 83 (2006) 819–822.
- [27] C.M. Whitehouse, R.N. Dreyer, M. Yamashita, J.B. Fenn, *Anal. Chem.* 57 (1985) 675–679.
- [28] J.B. Fenn, M. Mann, C.K. Meng, S.F. Wong, C.M. Whitehouse, *Science* 246 (1989) 64–71.
- [29] F.C. Gozzo, L.S. Santos, R. Augusti, C.S. Consorti, J. Dupont, M.N. Eberlin, *Chem. Eur. J.* 10 (2004) 6187–6193.
- [30] L.S. Santos, B.A.D. Neto, C.S. Consorti, C.H. Pavam, W.P. Almeida, F. Coelho, J. Dupont, M.N.E. Eberlin, *J. Phys. Org. Chem.* 19 (2006) 731–736.
- [31] G.W. Parshall, S.D. Ittel, *Homogeneous Catalysis*, Wiley, New York, 1992, pp. 269–296.
- [32] K.-H. Wolf, B. Kuster, H. Herlinger, C.-J. Tschang, E. Schrollmeyer, *Angew. Makromol. Chem.* 68 (1978) 23–37.