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Analysis of the Relationship between the Composition of a Bronsted Acidic Task-Specific Ionic Liquid: 1-(4-Sulfonic Acid)-butyl-3-Methylimidazolium Hydrogen Sulfate ([bsmim][HSO_4]), and Its Behavior on Reactive Systems †

María B. Martini [1], María V. Bravo [2] and Claudia G. Adam [2,*]

[1] IQAL (UNL-CONICET), Laboratory of Organic Physicochemistry, Faculty of Chemical Engineering, University National of Litoral; mbmartini@fiq.unl.edu.ar
[2] address; mvbravo@fiq.unl.edu.ar
* Correspondence: cadam@fiq.unl.edu.ar; Fax: +54-342-4571-162

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Abstract: Ionic liquids (IL) are proposed as an alternative to conventional organic solvents. Among them, there is a subgroup called "task specific ionic liquid" (TSIL), in which a functional group is covalently attached to the cation or to the anion. This is allows to "direct" towards a specific action its chemical properties in a reactive system. In recent years, the 1-(4-sulfonic acid)-3-methyl butylimidazolium [bsmim] with bisulfate counterion [HSO_4] is one of the most studied TSIL. This work aims to contribute to a better comprehension of the relationship between the structure of this TSIL and their catalytic behavior. The objective is to identify which part of the structure of the TSIL is responsible for the catalytic action observed in specific reactive systems and to understand how the addition of a functional group such as -SO_3H influences on the structure and therefore its behavior. The 1-butyl-3-methylimidazolium [bmim] was also synthesized with the same counterion. Both ILs were tested in two reactive systems: esterification reactions and synthesis of dibenzoxanthenes. The yields obtained were compared with respect to the action of sulfuric acid. Furthermore, cyclic voltammetry was used to identify the species present in the ILs. The results indicate that TSIL show an improved catalytic activity in both types of reactions in comparison with bmim HSO_4. The relationship between the voltammetric results and the final performance allowed to interpret the behavior of these ILs. The IL's synthesis and purification method influence on the species present which condition the results on the reactive system.

Keywords: task specific ionic liquids; esterification reaction; dibenzoxanthenes synthesis; catalysis

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1. Introduction

In recent years, the need for design and develop sustainable and environmentally friendly chemical processes has grown. Thus, ionic liquids (ILs) emerge as alternative catalysts and solvents for a wide variety of processes.

ILs have certain advantages over traditional molecular solvents, such as low vapor pressure, high catalytic activity, thermal stability, and the possibility of varying their structure to manipulate certain properties such as solubility and their behavior in different reactive systems [1–3].

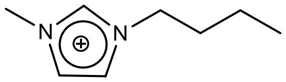
There is a new tendency to obtain greener ILs. Thus, a new route was emerged to design the so-called task specific ionic liquids (TSILs), in which a functional group is covalently attached to the cation or alternatively to the anion. In this direction, functionalized TSILs with a sulfonic acid group have been synthetized, offering a new possibility for bronsted acid catalysts that are more environmentally friendly. These TSILs allow the development of reactions with a phase transfer and the possibility of catalyst recovery and recycling.

The objective of our work is to relate the behavior of these TSILs in different reactive systems with their chemical structure. The aim is to optimize the selection of TSIL to achieve a specific property and analyze the effect of the decoration of structure of imidazolium cation with a sulfonic group. In this direction, the synthesis of a TSIL was developed by decorating the structure of the 1-butyl-3-methyl imidazolium (bmim) cation with an acid sulfonic group, to obtain 1-(4-sulfonic acid)-butyl-3-methyl imidazolium (bsmim), with bisulfate counterion [HSO_4]. Both ILs ([bsmim] [HSO_4] and [bmim] [HSO_4]) were characterized by cyclic voltammetry. This tool was used to identify the species present in ILs which are synthetized from strong acids [4]. According to what was observed and in order to correlate results, the ILs were applied in two reactive systems: synthesis of dibenzoxanthenes and esterification reactions. The results of both reactions are discussed and compared with respect to the yields obtained when sulfuric acid (H_2SO_4) was used.

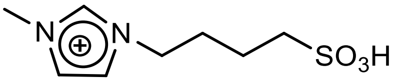
2. Methods

2.1. Synthesis of ILs

The synthesis of the ILs was carried out following the technique reported in our recently submitted work [5]. For the [bsmim] [HSO_4], 0.05 mol methyl imidazole and 0.05 mol of 1,4-butane sultone are placed in 7 mL MeOH into a round bottom flask with reflux and stirring, at 68 °C for 12 h. The solid obtained is washed four times with 5 mL of sulfuric ether and subsequently neutralized with H_2SO_4. For the [bmim] [HSO_4], 0.05mol of [bmim] [Br] and 0.05 mol of $NaHSO_4$, dissolved in 6 mL MeOH, are placed into a round bottom flask with reflux and stirring, for 72 h at 68 °C. The solid residue obtained is filtered, and the supernatant was placed in rotary evaporator. The chemical structures of the ILs studied in this work are presented in Figure 1, both with bisulfate counterion.



1-butyl-3-methyl-imidazolium

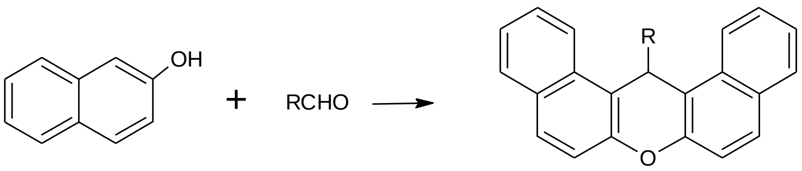


1-(4-sulfonic acid)-butyl-3-methylimidazolium

Figure 1. Structures of ILs analyzed.

2.2. Reaction of Dibenzoxanthenes

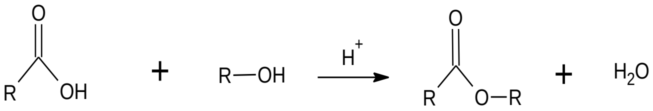
The general reaction is shown in Scheme 1. It is carried out by mixing 10 mmol of β-Naphthol, 5 mmol of aldehyde (benzaldehyde or 4-nitrobenzaldehyde) and 0.25 mmol of TSIL into a round bottom flask under reflux and agitation, during 2 h, at 100 °C. The reaction was monitored by silica gel TLC using Hexane/Acetate. After cooling to room temperature, 10 mL of water was added and the mixture was stirred for 5 min. The solid obtained was filtered, recrystallized using 10 mL of ethanol and dried in a vacuum pump. The purity of it was determined by IR spectroscopy and melting point.



Scheme 1. General reaction of synthesis of dibenzoxanthenes.

2.3. Esterification Reactions

The reactions (Scheme 2) were carried out into a round bottom flask under reflux and agitation, at 60 °C. 0.5 mmol of catalyst was added, using a 1:2 ratio of carboxylic acid/alcohol. The reaction was monitored by Gas Chromatography in a range of 1–24 h depending on the progress of the reaction, taking the constant area of the chromatographic peak corresponding to the product as a criterion. The product was quantified by the internal standard method using 1-bromo octane.



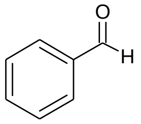
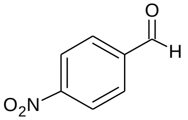
Scheme 2. General reaction of synthesis of esters.

3. Results

3.1. Obtaining Dibenzoxanthenes

Table 1 shows the percentage of yield obtained for each aldehyde used in both ILs and H_2SO_4.

Table 1. Results of synthesis of dibenzoxanthenes by ILs and H_2SO_4.

	Yield (%)		
RCHO	**H_2SO_4 [a]**	**bmim HSO_4**	**bsmim HSO_4**
	40	35	82
	59	20	70

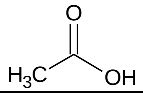
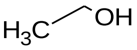
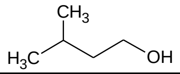
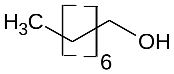
[a] 0.025mol of H_2SO_4 was used.

For both aldehydes used, the best yields were obtained for [bsmim] [HSO_4]. Since [bmim] [HSO_4] did not give good results with respect to TSIL in this type of reactions, only the recycling of [bsmim] [HSO_4] was evaluated. The catalyst was recovered from the reaction supernatant. It was taken to a rotary evaporator and dried in a vacuum pump. Then it was reused in another cycle without previous treatment. The yields obtained after four reaction cycles suffer a slight decrease. For dibenzoxanthene obtained from benzaldehyde, the yield drops from 82% to 74% in the fourth cycle.

3.2. Esterification Reactions

For this reaction, the carboxylic acid was kept fixed and the structure of the alcohol was varied. The yields obtained for both ILs and H_2SO_4 are shown in Table 2. For alcohols with MW less than 100 g/mol (ethanol-isoamyl alcohol) the average yield is 93.5% for both ILs and 73% for H_2SO_4, and for octanol the average yield was 51% compared to the 35% obtained for mineral acid.

Table 2. Results of synthesis of esters by ILs and H_2SO_4.

					Yield (%)	
Carboxylic acid	**Alcohol**	**Ester**	**H_2SO_4 [a]**	**[bmim][HSO_4]**	**[bsmim][HSO_4]**	**Time Reaction**
acetic acid 	ethanol 	1-ethyl acetate	62	91	94	2 h
	Isoamyl 	1-iso-amyl acetate	86	92	97	1 h
	octanol 	1-octyl acetate	35	48	57	24 h

[a] 0.015 mol of H_2SO_4 was used.

For both ILs, the formation of two phases was observed, one corresponding to the IL and the other to the product. As a consequence, these systems present the great advantage of recycling both catalysts. The esters produced show immiscibility in the ILs, therefore, the esterification begins as a homogeneous process and ends as two-phase (product and excess of reactant in the upper phase and the catalyst in the lower aqueous phase).

This differential solubility allows to facilitate the separation of the products by a simple decantation. Thus, it was possible to recycle and reuse the catalysts. The ILs were separated from the water produced during the synthesis. They were washed three times with ethyl acetate to eliminate remaining traces of the reaction. The results after four recycling cycles to obtain isoamyl acetate for each IL are shown in Table 3.

Table 3. Results of recycling of both ILs for synthesis of isoamyl acetate.

	Yield (%)	
Reaction Cycles	**[bsmim] [HSO_4]**	**[bmim] [HSO_4]**
1	97	92
2	96	80
3	96	75
4	91	64

3. Conclusions

The voltammetric results of TSIL, [bsmim] [HSO_4], indicate that in addition to the ionic pair, free H_2SO_4 of the autoprotolysis equilibrium is present, because the method of obtaining the TSIL involves a protonation equilibrium of the zwitterion (4-(1-methyl imidazolium-3-yl)-1-butane sulfonate (Zbsmim)) with H_2SO_4. On the other hand, for [bmim] [HSO_4], the bisulfate anion is forming part of the cation-anion ionic network in the IL's structure, so it would not be available to catalyze. In this case the catalysis could be due to the presence of the bisulfate sodium specie because the method of obtaining this IL involves the metathesis reaction between this salt and IL [bmim] [Br] (the voltametric results were recently sent for revision [5]). From the results observed in the reactive systems for both ILs, we can conclude that in general there is an increase in the yield between 15-30% for both reactions with respect to the action of the inorganic catalyst. The ILs are suitable for both systems. The TSIL [bsmim] [HSO_4] allows to obtain better performances in both reactive systems with the possibility of its recycling and reusing. This TSIL is a reservoir of H_2SO_4, available for controlled delivery according to the demand of the reactive systems.

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References

1. Rogers, R.D.; Seddon, K.R. *Ionic Liquids: Industrial Applications to Green Chemistry*; ACS Symposium Series; Washington, DC, USA, 2002.
2. Wasserscheid, P.; Keim, W. Ionic Liquids—New "Solutions" for Transition Metal Catalysis. *Angew. Chem. Int. Ed.* **2000**, *39*, 3772.
3. Rogers, R.D.; Seddon, K.R. Ionic Liquids–Solvents of the Future? *Science* **2003**, *302*, 792.
4. Bravo, M.V.; Fernández, J.L.; Adam, C.G.; Della Rosa, C.D. Understanding the Role of Protic Ionic Liquids (PILs) in Reactive Systems: Rational Selection of PILs for the Design of Green Synthesis Strategies for Allylic Amines and β-Amino Esters. *ChemPlusChem* **2019**, *84*, 919–926.
5. Martini, M.B.; Fernández, J.L.; Adam, C.G. *Toward Understanding the Catalytic Performance of Ionic Liquids (ILs) in Organic Synthesis—Voltammetric Characterization of Sulfonic Task-Specific ILs with Bisulfate Anions PCCP*; ID: CP-ART-10-2020-005674; November 2020; under review.