

Proceeding Paper

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] [HSO₄]), and Its Behavior on Reactive Systems [†]

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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 allows direction towards a specific action of its chemical properties in a reactive system. In recent years, 1-(4-sulfonic acid)-3-methyl butylimidazolium [bsmim] with bisulfate counterion [HSO₄] has been 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 its 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 -SO₃H influences the structure and therefore its behavior. 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 shows an improved catalytic activity in both types of reactions in comparison with bmim HSO₄. The relationship between the voltammetric results and the final performance allowed the interpretation of the behavior of these ILs. The IL synthesis and purification method influence on the present species and may affect the results of the reactive system.

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

1. Introduction

In recent years, the need for design and development of sustainable and environmentally friendly chemical processes has grown. Thus, ionic liquids (ILs) have emerged 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 has emerged to design 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 synthesized, offering a new possibility for

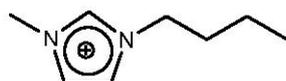
bronsted acid catalysts that are more environmentally friendly. These TSILs allow the development of reactions with a phase transfer and the possibility of catalyst recovery and recycling.

The objective of our work is to relate the behavior of these TSILs in different reactive systems to 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 the 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 $[\text{HSO}_4^-]$. Both ILs ($[\text{bsmim}] [\text{HSO}_4^-]$ and $[\text{bmim}] [\text{HSO}_4^-]$) were characterized by cyclic voltammetry. This tool was used to identify the species present in ILs which are synthesized from strong acids [4]. According to what was observed and 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.

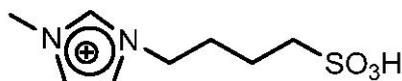
2. Methods

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 $[\text{bsmim}] [\text{HSO}_4^-]$, 0.05 mol methyl imidazole and 0.05 mol of 1,4-butane sultone were placed in 7 mL MeOH in a round-bottom flask with reflux and stirred, at 68 °C for 12 h. The solid obtained was washed four times with 5 mL of sulfuric ether and subsequently neutralized with H_2SO_4 . For the $[\text{bmim}] [\text{HSO}_4^-]$, 0.05 mol of $[\text{bmim}] [\text{Br}]$ and 0.05 mol of NaHSO_4 , dissolved in 6 mL MeOH, were placed into a round-bottom flask with reflux and stirred, for 72 h at 68 °C. The solid residue obtained was filtered, and the supernatant was placed in a rotary evaporator. The chemical structures of the ILs studied in this work were presented in Figure 1, both with bisulfate counterion.



1-butyl-3-methyl-imidazolium

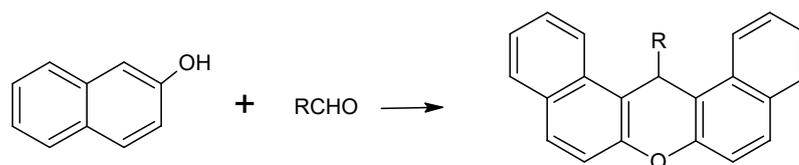


1-(4-sulfonic acid)-butyl-3-methylimidazolium

Figure 1. Structures of ILs analyzed.

2.2. Reaction of Dibenzoxanthenes

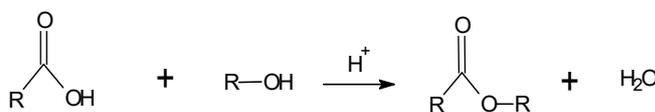
The general reaction is shown in Scheme 1. It was carried out by mixing 10 mmol of β -Naphthol, 5 mmol of aldehyde (benzaldehyde or 4-nitrobenzaldehyde), and 0.25 mmol of TSIL into a round-bottom flask under reflux and agitation, for 2 h, at 100 °C. The reaction was monitored by silica gel TLC plates 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 FT-IR spectroscopy and melting point.



Scheme 1. General reaction of synthesis of dibenzoxanthenes.

2.3. Esterification Reactions

The reactions (Scheme 2) were carried out in 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 for 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 .

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

^a 0.025 mol of H_2SO_4 was used.

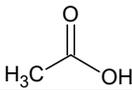
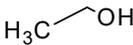
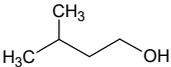
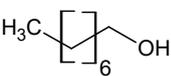
For both aldehydes used, the best yields were obtained for [bsmim] [HSO_4]. Since [bmim] [HSO_4] did not give good results with respect to TSIL in this type of reaction, only the recycling of [bsmim] [HSO_4] was evaluated. The catalyst was recovered from the reaction supernatant. It was taken to a rotary evaporator and dried in a vacuum pump. Then it was reused in another cycle without previous treatment. The yields obtained after four reaction cycles show 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 molecular weight less than 100 g/mol (ethanol-isoamyl alcohol), the average yield is

93.5% for both ILs and 73% for H₂SO₄, and for octanol the average yield was 51% compared to 35% obtained for mineral acid.

Table 2. Results of synthesis of esters by ILs and H₂SO₄.

Carboxylic Acid	Alcohol	Ester	Yield (%)			Time Reaction
			H ₂ SO ₄ ^a	[bmim][HSO ₄]	[bsmim][HSO ₄]	
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 H₂SO₄ was used.

For both ILs, the formation of two phases was observed, one corresponding to the IL and the other to the product. Consequently, 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 the facilitation of the separation of the products by 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.

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

4. Conclusions

The voltametric results of TSIL, [bsmim] [HSO₄] indicate that in addition to the ionic pair, free H₂SO₄ 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 H₂SO₄. On the other hand, for [bmim] [HSO₄], 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 of 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] [HSO₄] allows the obtaining of better performance in both reactive systems with the possibility of its recycling and reusing. This TSIL is a reservoir of H₂SO₄, available for controlled delivery according to the demand of the reactive systems.

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