

Ionic Liquids and Catalysis

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Esse documento analisa o crescimento do número de publicações que tratam do uso de líquidos iônicos (ILs) no período 1994-2013. A área da catálise é identificada como sendo a área pioneira e responsável para o brusco aumento do interesse pelo ILs. O mesmo é verdadeiro para a comunidade científica brasileira. As contribuições do grupo do Prof Roberto Fernando de Souza e as desenvolvidas através de numerosas colaborações estão descritas nesse contexto. O levantamento bibliográfico no período estudado mostra que o aumento significativo de publicações sobre ILs ocorre em momentos diferentes dependendo da área (catálise, energia, materiais, química analítica, biomassa, etc.).

This paper explores the growing number of publications concerning the use of ionic liquids (ILs) in the period from 1994 to 2013. Catalysis can be identified as the area responsible for the surge of interest in ILs. The same is true for the Brazilian scientific community. The contributions of the group of Prof Roberto Fernando de Souza and those obtained through numerous collaborations are described in this context. The literature survey shows that in the studied period the significant increase in ILs publications occurs at different times depending on their applied area (catalysis, energy, materials, analytical chemistry, biomass, etc.).

Keywords: ionic liquid, catalysis, Brazilian catalytic community

1. Introduction

Ionic liquids (ILs) are the subject of more than 45000 papers derived from numerous scientific areas. A chronologic report of the number of publications *per* year is reported to identify the factors that have set off this behavior. This manuscript investigates the role of the catalysis community on the growing interest for ILs; the case of the Brazilian community being specifically observed, including the contributions of the group of Prof Roberto Fernando de Souza [Prof Roberto de Souza (1958-2013) leader of the Laboratory of Reactivity and Catalysis from 1987; Institute of Chemistry of UFRGS (Federal University of Rio Grande do Sul), Porto Alegre, Brazil]. The present work does not aim at comprehensively reviewing applications of ILs: rather, it tries to highlight the interdisciplinary of their use. The latter is certainly an important factor that may allow the future development of even more interesting applications directed to technological innovation. Significant papers describing specific overviews

or new applications of ILs are reported to illustrate the importance of classical or emergent uses of ILs.

2. Ionic Liquids Publications

2.1. Ionic liquids: first descriptions and properties

The origin of IL can be found in the first description of the physicochemical properties of $[\text{EtNH}_3][\text{NO}_3]$, which has a melting point of 12 °C, published by Paul Walden in 1914.¹ An extract of this historical paper is reproduced in the very interesting review of Plechkova and Seddon.² As mentioned by Seddon, the current definition for ionic liquids is derived from Walden's observations: ionic liquids are most commonly defined as materials that are composed of cations and anions, which melt at or below 100 °C. Their relatively low viscosity is also commented to define them.³ From that date on, ILs were mentioned as alternative solvents mainly in electrochemistry (non aqueous electrolyte and large electrochemical window)⁴ and for applications in synthetic chemistry, making the object of a very small number of academic papers. Nevertheless,

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a real interest on the study and applications of ILs occurred at the end of the 90s,⁵ probably related to the involvement of industry that published several patents describing the potential use of ionic liquids for large scale green industrial processes (both catalytic and non-catalytic).² This set of occurrences induced the organization, in 2000, of the “Advanced Research Workshop”, sponsored by NATO, where academics and industrialists participate.

Welton⁶ lists the principal physical properties of ILs that permit them to be used as green solvent for synthesis and catalytic processes: (i) they are good solvents for a wide range of both inorganic and organic materials, and unusual combinations of reagents can be brought into the same phase; (ii) they are often composed of poorly coordinating ions, so they have the potential to be highly polar yet non-coordinating solvents; (iii) they are immiscible with a number of organic solvents and provide a non-aqueous, polar alternative for two-phase systems. Hydrophobic ionic liquids can also be used as immiscible polar phases with water. (iv) ionic liquids are nonvolatile, hence they may be used in high-vacuum systems and eliminate many containment problems.⁶ The set of these properties orientates naturally the application of ILs as alternative and sustainable solvents and more specifically as solvents in biphasic catalytic processes. The great flexibility of IL can be highlighted using imidazolium-based ILs as example (see Scheme 1). Their physicochemical properties can be adjusted by a suitable choice of cations and anions.⁷ To date the term “imidazolium” is included in the title of more than 2000 papers that describe the use of ILs, and more than 1300 times during the last five years.



Scheme 1.

2.2. Ionic liquids: electrochemistry and catalysis

Figure 1 reports the number of papers *per year* (1994-2013) where IL is mentioned as topic and for comparison also related to the electrochemical and catalysis area.

ILs were first mentioned in the literature related to electrochemistry, but the number of publications describing their use increased sharply since about 2000, as the interest for these compounds was investigated by the catalysis community. Figure 1 shows that the increase of papers describing the use of ILs in catalysis and electrochemistry contributes significantly to the overall growth for the interest of ILs and Figure 2 reports the percentage that

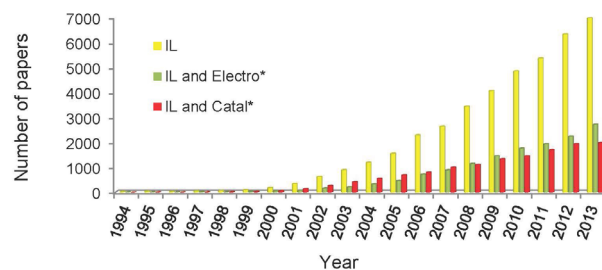


Figure 1. Increase of international IL publications (1996-2013) and those related to the electrochemical and catalysis areas.

each area, i.e., electrochemistry and catalysis, represent in the IL publications.

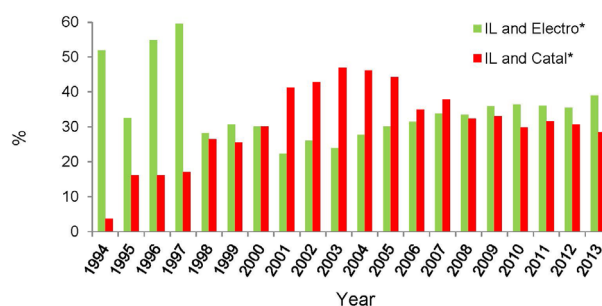


Figure 2. Proportion of IL publications from catalysis and electrochemical areas in the IL publications (1994-2013).

As deduced from Figure 2, the main contribution to IL papers was due to electrochemical studies until 1997; but, since then, catalysis leads regarding the new applications of IL. To date, both areas have equivalent importance in IL studies. However, data from 2010-2013 (Figure 1 and 2) indicates that the contribution of papers from the catalysis area tends to a relative decrease due to the emergence of novel scientific fields dealing with ILs.

2.3. Ionic liquids: interdisciplinarity

From 1994 to nowadays, about 200 review articles have been published to actualize and divulgate the advances and perspectives concerning the application of ILs. Figure 3 shows that such contributions have been steadily increasing.

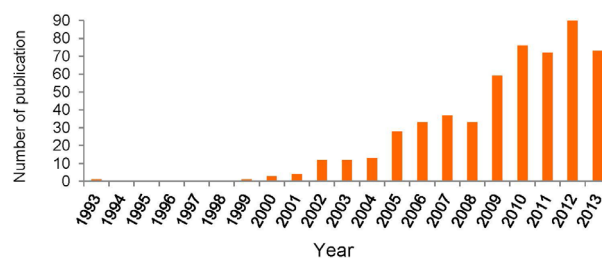


Figure 3. Increase of reviews on ILs (1994 to 2013).

This substantial production confirms that ILs attract a wide range of scientists across chemistry.

Besides those already cited, it is difficult to cite other specific areas of interest for ILs as many domains have emerged as overlapping with catalysis and electrochemistry. Some fields have been elected to evaluate how ILs, as a topic, became interesting during the period 1994–2013. As presented below, the choice of others areas is justified as it will be shown that each one has its own exponential curve beginning in different years. In the following, some examples are cited to illustrate how the use of ILs improves novel applications in each area. IL applications are related to the (i) “energy” area due to their use in electrochemical reactors (battery, capacitors, electrolyzer, fuel cell, etc.)⁸ and photocatalysis;⁹ (ii) “material” area due to their micellar organization¹⁰ or as immobilized compounds on or into polymers,¹¹ membranes,¹² electrodes,¹³ etc.; (iii) in the “nano-area” as they have the ability to design nano-materials,¹⁴ nano-composites¹⁵ or nano-particles;¹⁶ (iv) “biomass” area as they are currently employed in the transformation of sustainable sources to produce chemicals.¹⁷ In this field, it is interesting to report that the first patent related to ILs application was described in 1934 and claimed the use of halide salts of nitrogen-containing bases (such as 1-benzylpyridinium chloride, 1-ethylpyridinium chloride, etc.) to dissolve cellulose;¹⁸ (v) “analytical chemistry” area, as they are used as fillers of columns for chromatographic analysis¹⁹ or employed in microextraction processes²⁰ or to produce electrochemical sensors;^{21,22} (vi) enzymatic catalysis area to improve the performances of enzymatic reactions where the enzymes are solubilized in ILs to obtain a biphasic catalytic process.^{23,24} For reasons of order of magnitude, the results corresponding of several areas involving IL applications are reported in two different figures (Figure 4 and 5).

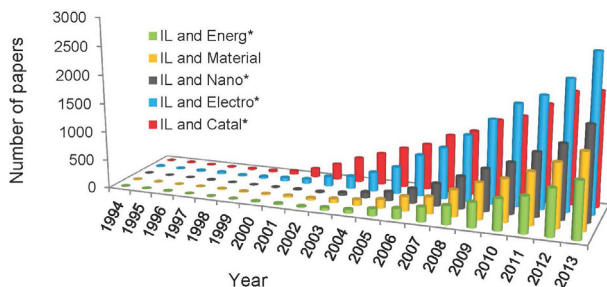


Figure 4. Increase in ILs publications in different areas (energy, material, nanotechnology or nanoscience and electrochemistry) (1994–2013).

Figure 4 reports data related to the areas of energy (Energ*), materials, nano-area (Nano*), electrochemistry (Electro*) and catalysis (Catal*), highlighting that in the

time period 1994–2013, more than 5000 papers in each area were published. Figure 5 displays data related to the areas of biomass, analytical chemistry (Analyt*), enzymatic catalysis (Enzym*), and biphasic processes (Biphas*). In the latter areas, the number of papers for each area amounts to approximately 1000 for the period 1994–2013. Figure 4 shows clearly that the catalysis area has been pioneer in the application of IL: this is the first research field registering an exponential increase, though electrochemists first used ILs. Just after, electrochemistry area witnessed the same phenomenon, and since 2008 more articles are published on the use of ILs in electrochemistry than in the area of catalysis, probably due to the emergence of new interdisciplinary studies.

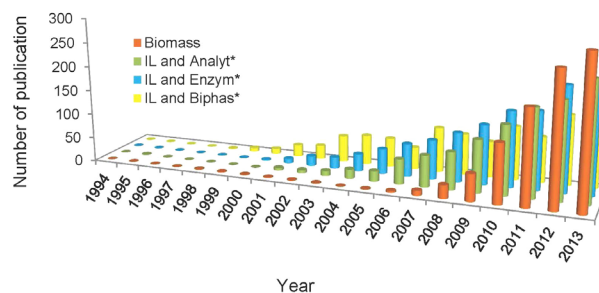


Figure 5. Increase of IL publications in different areas (biomass, analytical chemistry, enzymatic and biphasic) (1994–2013).

Energy (Energ*), materials and nano-area (Nano*) are important research fields involving ILs, benefiting from the results obtained from interface studies with catalysis and/or electrochemistry. It is to note that these other areas amount currently to a significant number of papers *per* year, with more than 1600, 1330 and about 1000 papers for the areas of Nano*, Material and Energ*, respectively in 1993. Except for catalysis, those reported in Figure 4 correspond to areas that are still increasing exponentially.

Figure 5 reports results of the same type of research that is recorded in Figure 4, but for domains that have registered about 1000 papers during the 1994–2013 period. For reasons of comparison, the researches include “Biphas*” to represent a topic belonging to traditional catalysis (in these studies, ILs are usually the solvents for organometallic catalytic species and reaction products are either insoluble in ILs or collected in another insoluble solvent) and that has been one of the first successful application of ILs in the 1990s. This area records also a total number of papers around 1000, as the others reported in Figure 5 (Biomass, Analyt* and Enzym*) that are the chosen specific topics.

One can note that the topic Biphas*, in comparison with the others reported in Figure 5, first shows an exponential growth chronologically, though this is now

a field of lesser interest. This is the reason why this area was chosen as representative of the catalysis area. Figure 5 evidences that specific areas such as Biomass, Analyt* and Enzym* initiated the inclusion of IL in their studies later in comparison to the classical application in catalysis (Biphas*). Again these results show that the classical area of catalysis, represented here by the Biphas* topic, is first at studying the use of IL.

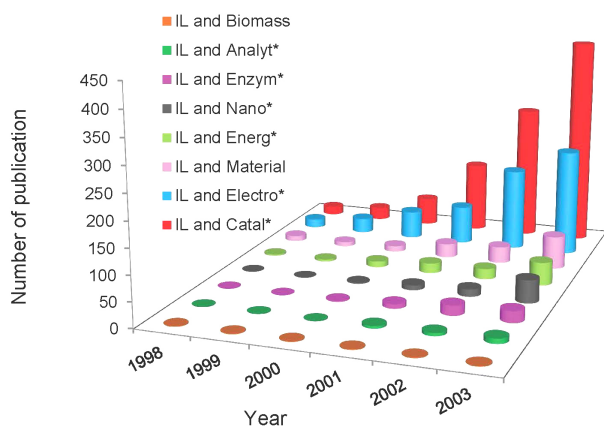


Figure 6. Increase of IL publications in different areas (energy, material, nanotechnology or nanoscience, electrochemistry biomass, analytical chemistry, enzymatic and biphasic) (1998-2003).

To evidence in detail how and when IL applications played an important role in several areas, an earlier and shorter period has been selected (1998-2003). The results are reported Figure 6. Figure 6 enables to visualize the beginning of the exponential growths of the topics selected before (Figure 4 and 5), as well as the magnitude of these increases. For Catal* and Electro*, the early growth can be placed in 2000, but the Catal* topic increased in a more pronounced way than the Electro* topic. Figure 6 evidences the chronological start of the other topics: Material and Energ* in 2001, Enzym* in 2002 and Nano* in 2003, the latter showing a very pronounced increase. It is interesting to note that IL applications in Analyt* and Biomass topics remain modest even in 2003. Figure 5 confirms that the importance of the use of IL in Analyt* and Biomass topics occurred later, in 2005 and 2008, respectively.

2.4. Ionic liquids: industrial interest

The number of filed patents *per year* in the period from 1994 to 2013 reported in Figure 7 indicates an exponentially increasing number corresponding to a sum higher than 6000. This result indicates that the newly disclosed applications have potential interest for industrial technology.

Industrialization of processes that employ IL can be illustrated by the following example. The Difasol process, that can be retro-fitted into existing Dimersol™ plants, is marketed by Axens, an Institut Français du Pétrole (IFP) subsidiary, and is described in Chauvin's Nobel lecture.²⁵

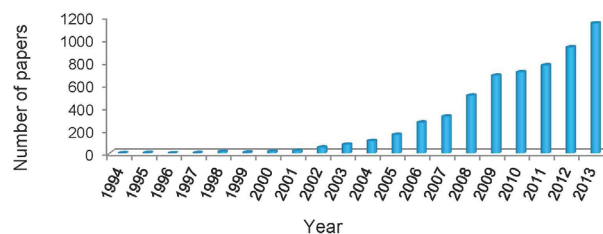


Figure 7. Increase of IL patents (1995-2013).

This process will be commented with a special attention later. The BASIL™ (biphasic acid scavenging) process, patented by BASF, is the most successful example of an industrial process using ionic liquid technology²⁶ and was awarded with the Institution of Chemical Engineers (IChemE) Award in 2005. In this process, triethylamine is replaced by 1-methylimidazole as an acid scavenger (HCl) to form the IL methylimidazolium chloride. At the end of the reaction, two clear liquids and easily separable phases are produced. The upper phase is constituted of the pure product (diethoxyphenylphosphine, a photoinitiator intermediate) and the lower phase is the pure IL that can be deprotonated with sodium hydroxide, regenerating the methylimidazole. The biggest industrial application of ILs to date is the ionylation process developed by PetroChina in which an aluminum(III)-based IL is used for alkylation of isobutene. This technology can be retro-fitted in an existing 65000 tons *per year* sulfuric acid alkylation plant in China.²⁷

3. Ionic Liquids and Brazilian Catalysis

Among the nearly 30,000 papers containing the term “Ionic Liquid*” in their title, the top five most cited have more than 2000 citations. The review written by Welton,⁸ describing the use of ILs as solvents for synthesis and catalysis, is the most cited, with more than 7500 citations. It has been referred to in more than 300 papers in 2014, clearly indicating the current interest of ILs in synthesis and catalysis. One of these most cited papers, published by Dupont, de Souza and Suarez⁷ illustrates that Brazilian scientists are considered as international specialists in the field of ILs, with more than 2700 citations.

Figure 8 reports the number of papers *per year* published by Brazilian research unities, involving the term IL and dealing with the use of ILs in catalysis. The total number of papers reported in Figure 8 related that the use of IL is

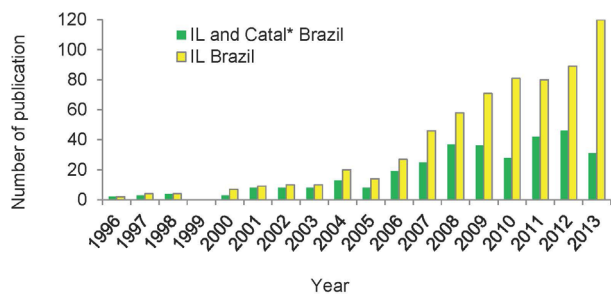


Figure 8. IL publications in catalysis with and without a Brazilian institution (1994 to 2013).

equal to 625. This significant number of studies expresses that Brazilian scientists presently contribute significantly to the ILs field as well as in the past. Moreover, it is interesting to observe in Figure 8 that only from 2009 a significant number of studies not related to catalysis have been published. It thus seems that in Brazil the interest for ILs was first awoken by the catalysis community and thereafter soon an area of interest to other researchers. This chronological effect is in line with the discussed above trend concerning international papers, i.e., ILs have been studied with more intensity first by the catalysis community and then their use expanded to other fields.

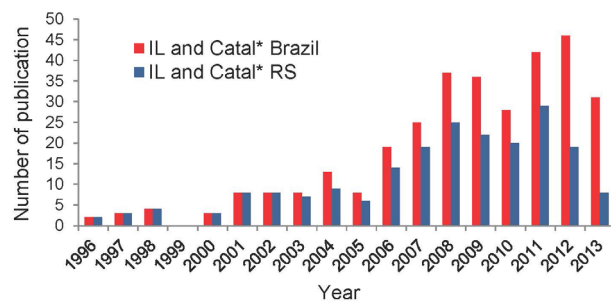


Figure 9. IL publications in the catalysis area, which for a Brazilian institution and also an institution located in the Rio Grande do Sul (RS) state, is involved (1994 to 2013).

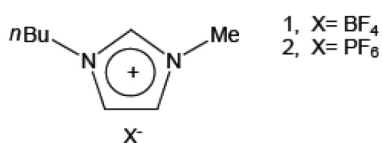
The number of papers *per year* with authors appointed to institutions located in the Rio Grande do Sul (RS) state was compared to those with authors belonging to other Brazilian institutions (Figure 9). From these data, it becomes clear that research groups from RS are accountable for a substantial number of published works from 1996 to 2011. This fact indicates that ILs as a topic was firstly adopted by RS researchers before spreading to other national institutions.

As described in many recent review articles, ILs have found their success in the 1990s due to their use in biphasic catalytic processes. As non miscible with organic solvents and with a very low vapor pressure, their use enables the transposition of homogeneous catalytic reactions in a heterogeneous environmentally friendly

process that enables catalyst reuse and avoids solvent distillation to recover the products. The Difasol process patented by IFP first in France²⁸ is certainly the main example of such innovation that ILs can provide. This process is an alternative version of DimersolTM process, also elaborated in IFP. The DimersolTM process is one of the first examples of the application of homogeneous catalysis in refining industry with more than 30 production units operating worldwide. Yves Chauvin from IFP (Yves Chauvin was awarded with the Nobel Prize in 2005 for having elucidated the metathesis mechanism) studying batteries electrolyte noted the use of ILs as a non-aqueous solvent (Yves Chauvin Nobel lecture).²⁵ As some of them also do not solubilize olefins, he employed ILs to turn the DimersolTM process heterogeneous, and then invented and developed the Difasol process, a biphasic process. This process has been the object of several patents filed in several countries.²⁹ Looking to the authors of these patents other than researchers at the IFP, Roberto Fernando de Souza, a Brazilian researcher of Federal University of Rio Grande do Sul (UFRGS) is one of the inventors.^{28,29}

The first meeting between Souza and Chauvin occurred in June 18th, 1987, when Chauvin was member of his doctorate thesis committee together with Wilhelm Keim among other members. It is worth noting that Chauvin and Keim were responsible for the invention and development of the Dimersol (IFP) and SHOP (Shell) processes respectively, illustrating how highly skilled and renowned was the evaluation committee of Souza. His doctoral supervisor was Prof I. Tkatchenko. Subsequently, Souza created, in 1987, his laboratory at the Institute of Chemistry of the UFRGS, in Porto Alegre, Brazil, where the main subject of investigation by his research group until 1993 was olefin oligomerization developed in homogeneous phase.³⁰ It is worth stressing that in 1993, ILs, as mentioned before, were a still mere curiosity that occasionally drew attention of some researchers, one of them being Yves Chauvin. In touch with him, Souza became convinced of the importance of the use of ILs as a new promising research topic and decided to send a student to perform complementary part of his doctorate at IFP (sandwich doctorate). One year after, Souza decided to spend a year at the IFP, developing studies of oligomerization in biphasic medium. At this time the group of Prof Chauvin concentrated their efforts on the butylmethylimidazolium aluminate organo-chloride IL, since it combined the advantages of alkyl aluminum compounds (a great area of expertise of Prof Chauvin with which, mixed with his extended knowledge on transition metal compounds, he designed and implemented a wide variety of industrial processes) and those of biphasic catalysis. The application of ILs in oligomerization catalysis was quickly recognized as

a successful approach. In early 1994, Souza then studied at the IFP the dimerization of butenes using dialkylimidazolium aluminates organo-chloride ILs, leading to the process DIFASOL, a biphasic variation for the industrial process of olefins dimerization marketed by IPF under the name Dimersol, as mentioned before. A set of data obtained on a laboratory scale enabled the study of the DIFASOL process in the IFP industrialization center.^{28,29} Back to Porto Alegre, Souza introduced a research line in biphasic catalysis employing new ILs formed by the 1-*n*-butyl-3-methyl imidazolium cation (BMI⁺) and inert anions such as tetrafluoroborate (BF₄⁻) and hexafluorophosphate (PF₆⁻), (Scheme 2). BMI.BF₄ and BMI.PF₆ show, respectively, a glass transition at -81 and -61 °C and are less reactive ILs when compared to those obtained by the combination of 1-*n*-butyl-methylimidazolium chloride and AlCl₃, which are air sensitive and these ILs were novel compounds, they have been very well-described and characterized³¹ and their introduction has altered the field of biphasic catalysis worldwide.



Scheme 2.

Table 1. Hydrogenation and/or asymmetric reactions conducted in biphasic system

Substrate	Medium ^a	Main product	Reference
Hydrogenation			
	[Ru]; BMI.BF ₄ ; ZnCl ₂		Dupont <i>et al.</i> ³⁴
Selective hydrogenation			
NBR ^b	[Ru]; BMI.BF ₄	HNBR	Müller <i>et al.</i> ³⁴
	[Co] or [Pd]; BMI.BF ₄	Butenes	Dupont <i>et al.</i> (2000) and Consorti <i>et al.</i> ³⁴
	[Pd]; BMI.BF ₄		Dupont <i>et al.</i> (2000) ³⁴
	[Pd]; BMI.BF ₄		Dupont <i>et al.</i> (2000) ³⁴
	[Pd]; BMI.BF ₄		Dupont <i>et al.</i> (2000) ³⁴
	[Pd]; BMI.BF ₄		Dupont <i>et al.</i> (2000) ³⁴
	[Pd]; BMI.BF ₄		Dupont <i>et al.</i> (2000) ³⁴
	[Pd]; BMI.BF ₄		Dupont <i>et al.</i> (2000) ³⁴

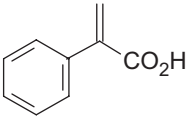
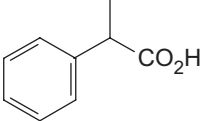
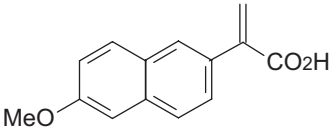
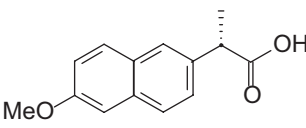
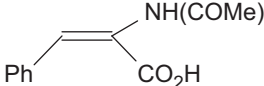
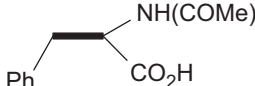
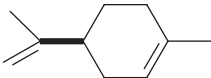
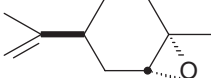
^a[M]: metal of the catalytic system; ^bacrylonitrile-butadiene rubber.

Publications concerning ILs provided Souza with some of the biggest hits in his career, with great emphasis on the publication, as co-author of a review article in the journal *Chemical Reviews*⁷ that, as of today, has harvested more than 2700 citations. This data is representative of his international leadership in this field of research, despite the high competition in the area.

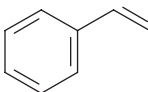
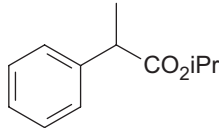

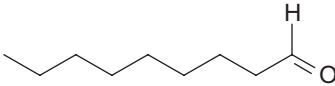
The reactions studied by Souza's group in biphasic systems were mainly the reactivity of olefin oligomerization using organochloraluminates ILs obtained by the combination of BMI.Cl; AlCl₃ and AlEt₂Cl₂.³² Several organometallic catalysts have been tested (mainly Ni(MeCN)₆][BF₄] but also cobalt complexes) using different ligand (bis(imino)pyridine and phosphine). The set of these studies evidences the influence of the molar ratio of BMI.Cl/AlCl₃/AlEt₂Cl₂ that modifies the acidity of the medium and, consequently, the catalytic properties (activity and selectivity) of each system.

BMI.BF₄ or BMI.PF₆ ILs have been employed by Souza to develop biphasic processes. The aim of these studies focused on the catalyst recycling by its easy separation from the reaction product by simple decantation using BMI.BF₄ or BMI.PF₆ ILs, more suitable solvent as they are not air sensitive. Examples of the cited reactions that have been developed by Souza's group and several collaborators are exemplified in Tables 1-5. For all these reactions, oligomerization³³ (see Table 4), hydrogenation




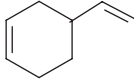
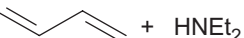
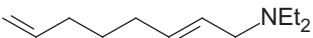
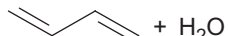
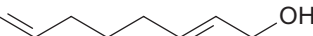
Table 2. Asymmetric hydrogenation and epoxidation conducted in biphasic system

Substrate	Medium ^a	Main product	Reference
Asymmetric hydrogenation			
	[Ru]; BMI.BF ₄		Monteiro <i>et al.</i> ³⁴
	[Ru]; BMI.BF ₄		Monteiro <i>et al.</i> ³⁴
	[Rh]; BMI.BF ₄		Berger <i>et al.</i> ³⁴
Asymmetric epoxidation of limonene			
	[Mn]; BMI.BF ₄ ; H ₂ O ₂		Pinto <i>et al.</i> ³⁹

^a[M]: metal of the catalytic system.**Table 3.** Hydroesterification of styrene and hydroformylation of 1-octene conducted in biphasic system



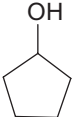
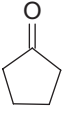
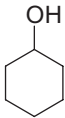
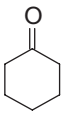
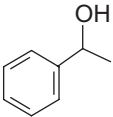
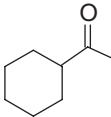
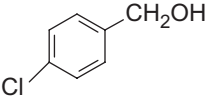
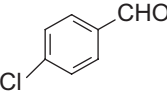
Substrate	Medium ^a	Main product	Reference
Hydroesterification of styrene			
	[Pd]; BMI.BF ₄ ; CO; ^b iPrOH		Zim <i>et al.</i> ³⁵
Hydroformylation of 1-octene			
	[Rh]; BMI.PF ₆ ; CO; H ₂		Dupont <i>et al.</i> ³⁶

^a[M]: metal of the catalytic system; ^bisopropanol.**Table 4.** Butadiene dimerization, cyclodimerization and telomerization and hydrodimerization conducted in biphasic system

Substrate	Medium ^a	Main product	Reference
Dimerization			
	[Pd]; BMI.X (X= BF ₄ ; PF ₆ ; CF ₃ SO ₃)		Silva <i>et al.</i> ³³
Cyclodimerization			
2 	[Fe]; BMI.BF ₄ or BMI.PF ₆		Ligabue <i>et al.</i> ³⁷
Telomerization			
2  + HNEt ₂	[Pd]; BMI.BF ₄		Pinto <i>et al.</i> ³⁹
2  + H ₂ O	[Pd]; BMI.BF ₄		de Souza <i>et al.</i> ³²

^a[M]: metal of the catalytic system.

Table 5. Alcohol oxidation catalyzed by ruthenium-based catalyst conducted in biphasic system using BMI.BF₄ IL and carried out under O₂ atmosphere, de Souza⁴¹

Substrate	Main product
	
	
	
	
	

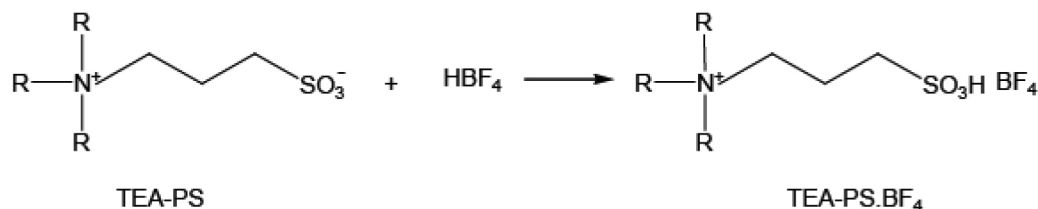
(selective and asymmetric)³⁴ (see Table 1 and 2), hydroesterification³⁵ (see Table 3), hydroformylation³⁶ (see Table 3), cyclodimerization³⁷ (see Table 4), polymerization³⁸ and epoxidation³⁹ (see Table 2), telomerization⁴⁰ (see Table 4) and oxidation⁴¹ (see Table 5), the catalysts systems were active in homogeneous conditions and showed in biphasic media equal or highest activities without modifying or enhancing the selectivity.

Based on an expertise acquired on the use of ILs and the diversification of applications that have been achieved with them, Souza opened new fields of investigation that determined the expansion of the activities of the group, especially in the field of fuel cells and their use in the area of clean energy. Based on characterization studies involving numerous collaborations⁴² of the ILs synthesized by the group and the urgent need to develop new technologies for the production (or transfer) of energy, a peculiar application of the use of ILs as agents of ionic conduction between the electrodes of fuel cells was developed. The corresponding results had a great impact in the area,⁴³ have been object of patents⁴⁴ and determine the expansion of the activities of the Souza group to the point of designing a laboratory of clean energy. Souza then initiated a new research line aiming using hydrogen as the main energetic vector in the Brazilian energetic platform (since Brazil holds an enormous hydroelectric capacity). According to him, the use of hydrogen produced at low cost would be an

alternative to diminish CO₂ emission produced by gasoline combustion. The main point leading Souza to propose hydrogen production by water electrolysis as a solution for Brazil (as hydrogen economy is limited by the cost of hydrogen production) was based on the potential use of the hydroelectric capacity of Brazilian facilities that is currently wasted. Wasted water corresponds to an excess amount of water that must be removed by the lock gates of the dams in order to decrease the reservoir volume and prevent overflow. Based on energy data corresponding to the year 2008 for Brazil, Souza showed, assuming that all wasted water would be used to produce electric energy: “The hydrogen produced with 106.2 TWh of wasted energy would be sufficient to replace all the gasoline consumed in 2008 and to avoid the generation of 5.70×10^7 ton of CO₂ emissions. Considering the cost of CO₂ capturing and the avoided environmental pollution, the hydrogen economy is viable in such a context”.⁴⁵ Thus, work with the production of hydrogen, mainly by electrolysis of water and with the use of hydrogen fuel cells employing ILs as electrolyte, became a new and promising research line of the group. As example, one of these studies showed that the addition of small quantities of BMI.BF₄ to water enables the production of pure hydrogen with high efficiency at room temperature and with inexpensive and available electrodes (nickel, molybdenum and iron alloys).⁴⁶ In the case of molybdenum electrode, the characterization of the double layer formed at the electrode/electrolyte interface evidenced that the imidazolium ring is strongly adsorbed on the electrode surface, explaining the synergy observed between molybdenum and the imidazolium electrolyte.⁴⁷ BMI.BF₄ also showed interesting application in capacitor.⁴⁸

Recently, the group proposed a new family of ILs, the tetra-alkyl-ammonium-sulfonic acid IL,⁴⁹ which are easily prepared from inexpensive reagents and whose cation presents both Lewis and Bronst ed acidity. Among them, the triethylammonium-propanesulfonic acid tetrafluoroborate (TEA-PS.BF₄) (see Scheme 3), when used as electrolyte in water electrolysis and showed improved performances in the hydrogen evolution reaction (HER) when compared with BMI.BF₄ and KOH. This behavior may result from the formation of channels organized by the intrinsic structure of the IL and their assemblage as TEA-PS is a zwitterionic species.⁵⁰

Regarding the use of ILs in the area of materials synthesis, the group proposed the synthesis of zeolites using BMI.Cl as structure directing agent.⁵¹ Depending on the Si/Al ratio of the medium, different structures as well as aggregates format of various size are obtained (ZSM-5 or β -zeolite). More recently, ILs were employed to synthesize ordered mesoporous ZSM-5 materials, a strategy to enhance



Scheme3.

the diffusion of large molecules through a mesoporosity to attain acid sites located at the entry of microporosity.⁵²

The last area involving the use of ILs that Souza pioneered in his laboratory is that of green chemistry. Souza contributed to the application of two patents in Brazil, corresponding to the production of olefins by means of dehydration of light alcohols⁵³ and the synthesis of cyclic carbonates using CO₂ as reactant and catalysts containing ILs.⁵⁴ In this special issue, a study describing the synthesis of 5-hydroxymethylfurfural via dehydration of fructose and glucose using ILs is also an example of the contribution of the group of Souza to green chemistry involving ILs.

It can be stated that the topic of ILs is certainly important for the Brazilian catalysis community, highlighted by its present strength, which can be attributed to the opportunity that had to be seized and that Souza seized when he chose to work with Y. Chauvin in 1994. Back to Brazil, Souza shared immediately his knowledge with his colleagues. Today, one can measure the magnitude of his legacy.

4. Ionic Liquids: Industrial Interest

To illustrate that processes involving ILs have an industrial potential in Brazil, Figure 10 reports the number of patents involving the use of ILs filed in Brazil by various countries. The set of these patents amounts to 96 demonstrating the importance of this topic from the industrial point of view. Moreover, this Figure 10 shows that Brazil, with almost 30% of the filed patents, occupies the second place after the USA (35%) together with the set of European countries (30%).

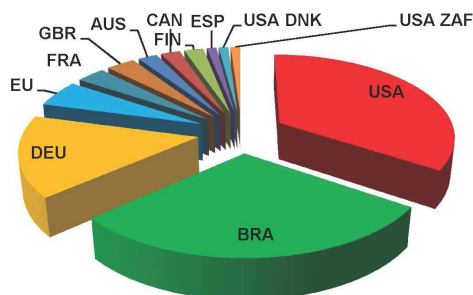


Figure 10. Filed patents in Brazil by different countries (1995-2013).

Conclusion

ILs represent a family of countless compounds. Though first described in the beginning of the 20th century, it is only at the end of the century that ILs experienced an unprecedented success in both the academic and industrial community. It is important to stress out that this success corresponded to the encounter of two areas of knowledge, electrochemistry and catalysis, with the latter pioneering and triggering the development of important IL applications. In Brazil, catalysis was also the starting point to study various interesting applications related to ILs. Today, novel thematic interfaces are the keys for future discoveries and applications, including for catalysis.

Since there are 10¹⁸ possible combinations of ILs due to the ability to interchange their corresponding cationic/anionic moieties,⁵⁵ it is possible to imagine that Brazil, with the expertise of its scientists,^{7,56} its chemical industry and with new governmental incentives for innovation, will be able to develop industrial technologies or new materials involving ILs. This contribution aimed at showing that we, as scientists, and in particular, as members of the catalysis community, still have opportunities to seize, such as to explore the potential of ILs for future sustainable technological solutions.

Supplementary Information

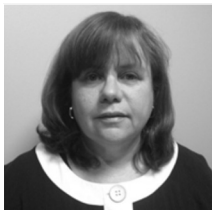
Supplementary data are available free of charge at <http://jbcs.sbq.org.br> as PDF file.

Acknowledgements

I would like to thank all colleagues and students who participated to the huge contribution of Professor Roberto Fernando de Souza during his too short scientific career.

No words can express my admiration and my gratitude to Roberto Fernando de Souza, my husband, father of our two sons and my scientific partner, who left us too early. This work is an homage to you, Roberto, as I know how both areas, IL and catalysis have been extremely important to you. If people are still with us as long as we remember

them, I hope that this humble work will help to perpetuate your remembrance and legacy as scientist and of the great person you were.



Michèle Oberson de Souza is Associated Professor at the Department of Physical-Chemistry of the Institute of Chemistry at the Federal University of Rio Grande do Sul (UFRGS) in Porto Alegre, where she develops her

research since 1987. Her main research interests concern the conversion of light olefin oligomerization and polymerization, reactions catalyzed by heterogenized organometallic systems to improve the production of linear and/or terminal oligomers and special polymers, respectively. The grafting of active species onto inorganic nano-structured materials and the development of biphasic processes using ionic liquids are then studied. She is presently co-coordinator of the Laboratory of Reactivity and Catalysis that was until 2013/11/29 headed by Prof Roberto Fernando de Souza.

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