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Chapter 15

New Brønsted Ionic Liquids: Synthesis, Thermodinamics and Catalytic Activity in Aldol Condensation Reactions

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Additional information is available at the end of the chapter

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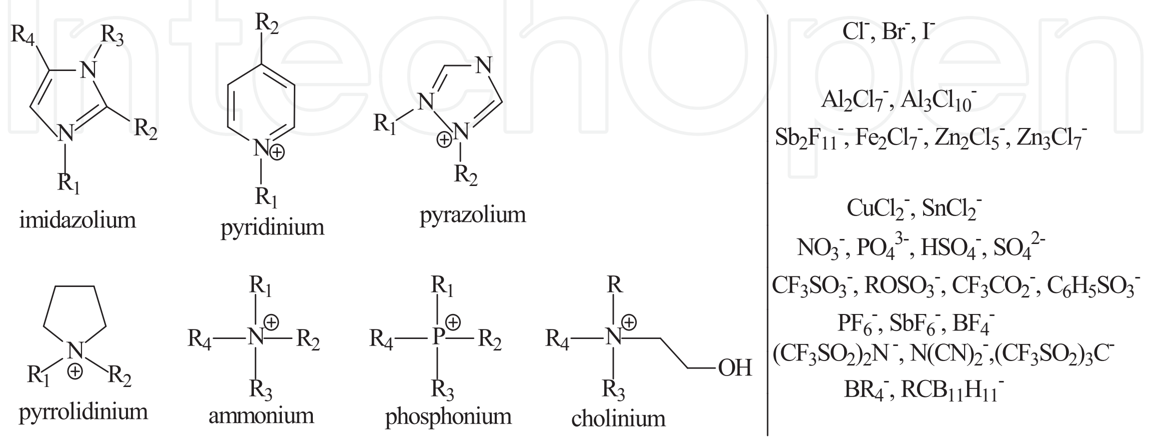
1. Introduction

It is a continuous challenge to find new catalysts able to perform with good activities and selectivity condensation reactions for the synthesis of pharmaceutical and fine chemicals. In the last years room temperature ionic liquids (ILs) have received a lot of interest as environmental friendly or "green" alternatives to conventional molecular solvents. They differ from molecular solvents by their unique ionic character and their "structure and organization" which can lead to specific effects [1].

Room-temperature ILs have been used as clean solvents and catalysts for green chemistry, stabilizing agents for the catalysts or intermediates, electrolytes for batteries, in photochemistry and electrosynthesis etc [2-6]. Their success as environmental benign solvents or catalysts is described in numerous reactions [7-11], such as Diels-Alder reactions [12, 13], the Friedel-Crafts reaction [14-17], esterification [18-20], cracking rections [21], and so on. The link between ionic ILs and green chemistry is related to the solvent properties of ILs. Some of the properties that make ILs attractive media for catalysis are: they have no significant vapour pressure and thus create no volatile organic pollution during manipulation; ILs have good chemical and thermal stability, most ILs having liquid ranges for more than 300^0C; they are immiscible with some organic solvents and therefore can be used in two-phase systems; ILs polarity can be adjusted by a suitable choice of cation/anion; they are able to dissolve a wide range of organic, inorganic and organometallic compounds; ILs are often composed of weakly coordinating anions and therefore have the potential to be highly polar.

The number of ILs has increased exponentially in the recent years. Many of them are based on the imidazolium cation and in a lesser proportion, alkyl pyridiniums and trialkylamines (Scheme 1). By changing the anion or the alkyl chain of the cation, a wide variety of ILs may be designed for specific applications. They can be of hydrophobic or hydrophilic nature depending on the chemical structures involved.



Scheme 1. Main cations and anions described in literature [1].

ILs can be divided into two broad categories: aprotic ionic liquids (AILs) and protic ionic liquids (PILs).

AILs largely dominate the open literature due to their relative inertness to organometallic compounds and their potential of applications, particularly in catalysis. They are synthesized by transferring an alkyl group to the basic nitrogen site through S_N2 reactions [1].

PILs are formed through proton transfer from a Brønsted acid to a Brønsted base. Recently there has been an increasing interest in PILs due to their greater potential as environmental friendly solvents and promising applications. Moreover, they present the advantage of being cost-effective and easily prepared as their formation does not involve the formation of residual by-products. A specific feature of the PILs is that they are capable of developing a certain hydrogen bonding potency, including proton acceptance and proton donation and they are highly tolerant to hydroxylic media [22-23].

The application of new policies on terms of environment, health and safety deals towards minimizing or substituting organic volatile solvents by green alternatives, placing a renewed emphasis on research and development of lesser harmful compounds as ILs. On the other hand, recently the interest in the use of PILs to tailor the water properties for cleaning applications in processes of minimization of CO_2/SO_2 emissions has increased [24-26].

In the last years numerous studies report the use of ILs as selective catalysts for different reactions, like aldol condensation reactions where several ILs have been successfully applied as homogeneous and heterogeneous catalysts [27-30]. Abelló et al. [28] described the use of choline hydroxide as basic catalyst for aldol condensation reactions between several ketones and aldehydes. Better conversions and selectivities were obtained when compared to other well-known catalysts, such as rehydrated hydrotalcites, MgO and NaOH. In addition, higher performance was obtained when choline was immobilized on MgO.

Zhu et al. [27] described the use of 1,1,3,3-tetramethylguanidine lactate ([TMG] [Lac]) as recyclable catalyst for direct aldol condensation reactions at room temperature without any solvent. It was demonstrated that for each reaction only the aldol adduct was produced when the molar ratio of the IL and substrate was smaller than 1. Moreover, after the reaction the IL was easily recovered and recycled without considerably decrease of activity.

Kryshtal et al. [29] described the application of tetraalkylammonium and 1,3-dialkylimidazolium perfluoro-borates and perfluoro-phosphates as recoverable phase-transfer catalysts in multiphase reactions of CH-acids, in particular in solid base-promoted cross-aldol condensations. The catalysts retained their catalytic activity over several reaction cycles.

In the study of Lombardo et al. [30] two onium ion-tagged prolines, imidazolium bis (trifluoromethylsulfonyl)imide-substituted proline and butyldimethylammonium bis (trifluoromethylsulfonyl) imide-substituted proline, were synthesized and their catalytic activity in the direct asymmetric aldol condensation was studied. The catalytic protocol developed by this group makes use of a 6-fold lower amount of catalyst with respect to the preceding reports [31, 32] and affords greater chemical yields and higher enantioselectivity.

The main objective of this chapter is to develop and study the applications of a new family of ILs based on substituted amine cations of the form RNH_3^+ combined with organic anions of the form $R'COO^-$ (being of different nature R and R'). The variations in the anion alkyl chain, in conjunction with the cations, lead to a large matrix of materials.

This kind of compounds show interesting properties for industrial use of ILs: low cost of preparation, simple synthesis and purification methods. Moreover, the very low toxicity and the degradability of this kind of ILs have been verified. Thus, sustainable processes can be originated from their use.

Recently, many studies dealing with the application of ILs in organic synthesis and catalysis have been published, pointing out the vast interest in this type of compounds [33-36]. With these facts in mind, we studied their catalytic potential for two condensation reactions of carbonyl compounds. The products obtained from these reactions are applied in pharmacological, flavor and fragrance industry.

2. Experimental

2.1. Preparation of ILs and supported ILs

The ILs synthesized in this work are: 2-hydroxy ethylammonium formate (2-HEAF), 2-hydroxy ethylammonium acetate (2-HEAA), 2-hydroxy ethylammonium propionate (2-HEAP), 2-hydroxi ethylammonium butanoate (2-HEAB), 2-hydroxi ethylammonium isobutanoate (2-HEAiB) and 2-hydroxi ethylammonium pentanoate (2-HEAPE).

The amine (Merck Synthesis, better than 99%) was placed in a three necked flask all-made-in-glass equipped with a reflux condenser, a PT-100 temperature sensor for controlling temperature and a dropping funnel. The flask was mounted in a thermal bath. A slight heating is necessary for increasing miscibility between reactants and then allow reaction. The organic acid (Merck Synthesis, better than 99%) was added drop wise to the flask under stirring with a magnetic bar. Stirring was continued for 24 h at laboratory temperature, in order to obtain a final viscous liquid. Lower viscosity was observed in the final product by decreasing molecular weight of reactants. No solid crystals or precipitation was noticed when the liquid sample was purified or stored at freeze temperature for a few months after synthesis. The reaction is a simple acid–base neutralization creating the formiate, acetate, propionate, butanoate, isobutanoate or pentanoate salt of ethanolamine that in a general form should be expressed as follows:

$$(HOCH_2CH_2)NH_2 + HOOCR \rightarrow (HOCH_2CH_2)NH_3^{+}(^{-}OOCR) \quad (1)$$

For example, when formic acid is used this equation shows the chemical reaction for the reactants ethanolamine + formic acid, with 2-HEAF as neutralization product.

Because these chemical reactions are highly exothermic, an adequate control of temperature is essential throughout the chemical reaction; otherwise heat evolution may produce the dehydration of the salt to the corresponding amide, as in the case for nylon salts (salts of diamines with dicarboxy acids).

As observed in our laboratory during IL synthesis, dehydration begins around 423.15 K for the lightest ILs. The color varied in each case from transparent to dark yellow when the reaction process and purification (strong agitation and slight heating for the vaporization of residual non-reacted acid for at least for 24 h) were completed.

There was no detectable decomposition for the ILs studied here when left for over 12 months at laboratory temperature. Less than 1% amide was detected after this period of time. On the basis of these results it appears obvious that the probability of amide formation is low for this kind of structures.

In order to obtain the supported ILs, 1 g of IL was dissolved in 7 ml of ethanol and after stirring at room temperature for 30 min, 1 g of alanine (Fluka, better than 99%) was added. The mixture was stirred for 2 h and then heated at 348 K under vacuum to remove ethanol. The supported ILs thus obtained were labelled hereafter as a-ILs.

2.2. Spectroscopy test

FT-IR spectrum was taken by a Jasco FT/IR 680 plus model IR spectrometer, using a NaCl disk.

2.3. Physical properties equipment

During the course of the experiments, the purity of ILs was monitored by different physical properties measurements. The pure ILs were stored in sun light protected form, constant

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humidity and low temperature. Usual manipulation and purification in our experimental work was applied [22].

The densities and ultrasonic velocities of pure components were measured with an Anton Paar DSA-5000 vibrational tube densimeter and sound analyzer, with a resolution of 10^{-5} g cm^{-3} and 1 m s^{-1}. Apparatus calibration was performed periodically in accordance with provider's instructions using a double reference (millipore quality water and ambient air at each temperature). Accuracy in the temperature of measurement was better than $\pm 10^{-2}$ K by means of a temperature control device that apply the Peltier principle to maintain isothermal conditions during the measurements.

The ion conductivity was measured by a Jenway Model 4150 Conductivity/TDS Meter with resolution of 0.01μS to 1 mS and accuracy of ±0.5% at the range temperature. The accuracy of temperature into the measurement cell was ±0.5 °C.

2.4. Catalytic studies

The studied reactions were the condensation between citral and acetone and between benzaldehyde and acetone. The reactions were performed in liquid phase using a 100 mL batch reactor equipped with a condenser system. To a stirred solution of substrate and ketone (molar ratio ketone/substrate = 4.4) was added 1 g of IL, and the flask was maintained at 333 K using an oil bath. Samples were taken at regular time periods and analyzed by gas chromatography using a flame ionization detector and an AG Ultra 2 column (15 m x 0.32 mm x 0.25 μm). Tetradecane was used as the internal standard. Reagents were purchase from Aldrich and used without further purification.

In order to separate the ILs from the reaction mixture, at the end of the reaction 6 mL of H_2O were added. The mixture was stirred for 2 h and then left 15 h to repose. Two phases were separated: the organic phase which contains the reaction products and the aqueous phase which contains the IL. In order to separate the IL, the aqueous phase was heated up to 393 K under vacuum.

3. Results and discussion

As Figure 1 shows, the broad band in the 3500-2400 cm^{-1} range exhibits characteristic ammonium structure for all the neutralization products. The OH stretching vibration is embedded in this band. The broad band centered at 1600 cm^{-1} is a combined band of the carbonyl stretching and N-H plane bending vibrations. FT-IR results clearly demonstrate the IL characteristics of compounds synthesized in this work.

Due to space considerations, we will present the thermodynamic properties only for two of the studied ILs: 2-HEAF and 2-HEAPE.

The molar mass and experimental results at standard condition for 2-HEAF and 2-HEAPE are shown in Table 1.

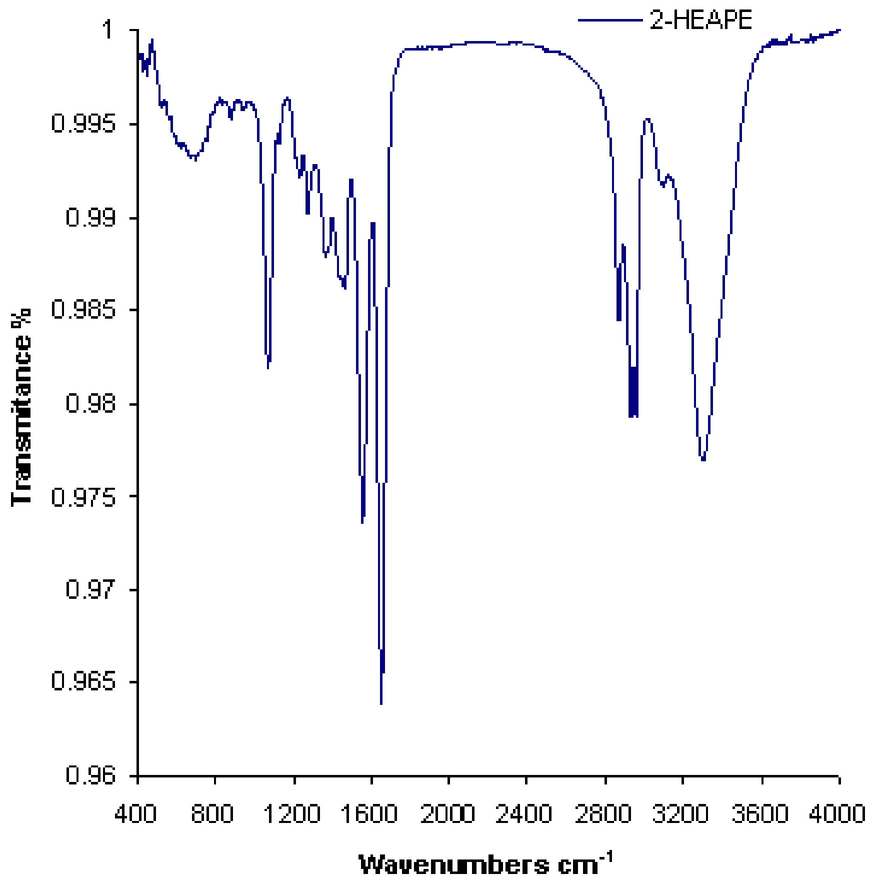

Figure 1. FT-IR spectrum for 2-HEAPE.

IL	Molecular Weight ($g\bullet mol^{-1}$)	Exp. Density ($g\bullet cm^{-3}$)	Exp. Ultrasonic Velocity (ms^{-1})	Exp. Conductivity ($\mu S\bullet cm^{-1}$)
2-HEAF	107.11	1.176489	1709.00	4197.6
2-HEAPE	163.21	1.045479	1591.59	239.6

[a]Other experimental data for comparison are not available from the literature.

Table 1. Experimental data for pure ionic liquids at 298.15 K and other relevant information[a]

The densities, ultrasonic velocities and isobaric expansibility of 2-HEAF and 2-HEAPE are given in Table 2, and the ionic conductivities are given in Table 3. From the results obtained it can be observed that an increase in temperature diminishes the interaction among ions, lower values of density and ultrasonic velocity being gathered for rising temperatures in each case.

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2-hydroxy ethylammonium formate (2-HEAF)									
T (K)	ρ (gcm⁻³)	u (ms⁻¹)	κ_S (TPa⁻¹)	$10^3 \cdot \alpha$ (K⁻¹)	T (K)	ρ (gcm⁻³)	u (ms⁻¹)	κ_S (TPa⁻¹)	$10^3 \cdot \alpha$ (K⁻¹)
338.15	1.148091	1613.59	334.53	0.6188	327.16	1.155890	1639.38	321.90	0.6148
337.90	1.148254	1614.14	334.26	0.6187	326.91	1.156069	1639.97	321.62	0.6147
337.66	1.148433	1614.71	333.97	0.6186	326.66	1.156247	1640.57	321.34	0.6146
337.40	1.148608	1615.30	333.67	0.6185	326.41	1.156426	1641.16	321.06	0.6145
337.15	1.148785	1615.87	333.39	0.6184	326.16	1.156603	1641.75	320.78	0.6144
336.91	1.148963	1616.46	333.09	0.6183	325.91	1.156780	1642.34	320.50	0.6143
336.66	1.149139	1617.04	332.80	0.6182	325.65	1.156957	1642.94	320.21	0.6142
336.41	1.149316	1617.63	332.51	0.6182	325.40	1.157136	1643.53	319.93	0.6141
336.16	1.149494	1618.22	332.21	0.6181	325.16	1.157314	1644.12	319.66	0.6140
335.90	1.149669	1618.81	331.92	0.6180	324.90	1.157490	1644.72	319.37	0.6139
335.65	1.149848	1619.38	331.64	0.6179	324.65	1.157669	1645.32	319.09	0.6138
335.40	1.150027	1619.96	331.35	0.6178	324.40	1.157846	1645.91	318.81	0.6137
335.16	1.150205	1620.55	331.05	0.6177	324.15	1.158023	1646.50	318.54	0.6136
334.90	1.150384	1621.13	330.77	0.6176	323.90	1.158201	1647.09	318.26	0.6135
334.66	1.150560	1621.71	330.48	0.6175	323.65	1.158378	1647.68	317.98	0.6134
334.40	1.150740	1622.30	330.19	0.6174	323.40	1.158556	1648.28	317.70	0.6133
334.16	1.150916	1622.89	329.90	0.6173	323.15	1.158734	1648.90	317.42	0.6132
333.90	1.151094	1623.48	329.61	0.6173	322.90	1.158910	1649.47	317.15	0.6131
333.65	1.151271	1624.06	329.32	0.6172	322.66	1.159088	1650.06	316.87	0.6130
333.41	1.151449	1624.64	329.03	0.6171	322.41	1.159265	1650.66	316.59	0.6129
333.16	1.151625	1625.23	328.75	0.6170	322.16	1.159442	1651.25	316.32	0.6128
332.90	1.151804	1625.82	328.46	0.6169	321.91	1.159620	1651.85	316.04	0.6127
332.65	1.151981	1626.41	328.17	0.6168	321.65	1.159797	1652.43	315.77	0.6126
332.41	1.152159	1626.99	327.88	0.6167	321.40	1.159976	1653.03	315.49	0.6125
332.15	1.152338	1627.58	327.59	0.6166	321.15	1.160154	1653.63	315.22	0.6124
331.90	1.152514	1628.16	327.31	0.6165	320.91	1.160330	1654.22	314.94	0.6124
331.65	1.152694	1628.75	327.02	0.6164	320.66	1.160509	1654.81	314.67	0.6123
331.40	1.152871	1629.34	326.74	0.6163	320.40	1.160688	1655.41	314.39	0.6122
331.16	1.153048	1629.93	326.45	0.6162	320.15	1.160863	1656.01	314.12	0.6121
330.90	1.153225	1630.52	326.16	0.6162	319.90	1.161042	1656.60	313.85	0.6120
330.65	1.153405	1631.11	325.88	0.6161	319.65	1.161218	1657.19	313.58	0.6119
330.41	1.153582	1631.69	325.59	0.6160	319.40	1.161398	1657.79	313.30	0.6118

330.15	1.153761	1632.29	325.30	0.6159	319.15	1.161574	1658.39	313.03	0.6117
329.90	1.153939	1632.88	325.02	0.6158	318.91	1.161750	1658.98	312.76	0.6116
329.65	1.154114	1633.47	324.73	0.6157	318.65	1.161930	1659.58	312.48	0.6115
329.41	1.154294	1634.06	324.45	0.6156	318.40	1.162110	1660.18	312.21	0.6114
329.15	1.154469	1634.65	324.17	0.6155	318.16	1.162286	1660.78	311.93	0.6113
328.91	1.154648	1635.24	323.88	0.6154	317.90	1.162462	1661.37	311.67	0.6112
328.65	1.154826	1635.84	323.59	0.6153	317.65	1.162643	1661.97	311.39	0.6111
328.40	1.155003	1636.43	323.31	0.6152	317.41	1.162820	1662.56	311.12	0.6110
328.15	1.155181	1637.02	323.03	0.6151	317.15	1.162998	1663.16	310.85	0.6109
327.90	1.155360	1637.61	322.75	0.6150	316.91	1.163174	1663.75	310.58	0.6108
327.66	1.155535	1638.20	322.47	0.6149	316.65	1.163352	1664.35	310.31	0.6107
316.15	1.163706	1665.55	309.77	0.6105	303.90	1.172408	1695.01	296.88	0.6054
315.90	1.163885	1666.15	309.50	0.6104	303.65	1.172587	1695.62	296.62	0.6053
315.65	1.164062	1666.74	309.23	0.6103	303.40	1.172764	1696.23	296.36	0.6052
315.40	1.164240	1667.34	308.96	0.6102	303.15	1.172937	1696.81	296.11	0.6051
315.15	1.164417	1667.94	308.70	0.6101	302.90	1.173120	1697.43	295.85	0.6050
314.90	1.164597	1668.54	308.43	0.6100	302.65	1.173295	1698.04	295.59	0.6049
314.65	1.164774	1669.14	308.16	0.6099	302.40	1.173473	1698.64	295.34	0.6048
314.40	1.164951	1669.73	307.89	0.6098	302.15	1.173648	1699.25	295.09	0.6047
314.15	1.165128	1670.33	307.63	0.6097	301.90	1.173826	1699.86	294.83	0.6046
313.90	1.165305	1670.94	307.35	0.6096	301.65	1.174003	1700.47	294.57	0.6045
313.65	1.165485	1671.54	307.09	0.6095	301.40	1.174180	1701.07	294.32	0.6043
313.40	1.165661	1672.13	306.82	0.6094	301.15	1.174361	1701.68	294.06	0.6042
313.15	1.165839	1672.72	306.56	0.6093	300.90	1.174535	1702.29	293.81	0.6041
312.90	1.166018	1673.34	306.29	0.6092	300.65	1.174714	1702.90	293.56	0.6040
312.65	1.166194	1673.94	306.02	0.6091	300.40	1.174891	1703.50	293.30	0.6039
312.40	1.166372	1674.54	305.75	0.6090	300.15	1.175070	1704.12	293.05	0.6038
312.15	1.166549	1675.14	305.49	0.6089	299.90	1.175247	1704.73	292.79	0.6037
311.90	1.166726	1675.74	305.22	0.6088	299.65	1.175425	1705.33	292.54	0.6036
311.65	1.166903	1676.34	304.96	0.6086	299.40	1.175602	1705.95	292.29	0.6035
311.40	1.167085	1676.95	304.69	0.6085	299.15	1.175780	1706.55	292.04	0.6034
311.15	1.167260	1677.55	304.43	0.6084	298.90	1.175955	1707.16	291.78	0.6033
310.90	1.167437	1678.14	304.17	0.6083	298.65	1.176133	1707.77	291.53	0.6032
310.65	1.167617	1678.74	303.90	0.6082	298.40	1.176311	1708.39	291.28	0.6030

310.40	1.167794	1679.35	303.63	0.6081	298.15	1.176489	1709.00	291.02	0.6029
310.15	1.167970	1679.94	303.38	0.6080	297.90	1.176666	1709.61	290.77	0.6028
309.90	1.168149	1680.55	303.11	0.6079	297.65	1.176842	1710.22	290.52	0.6027
309.65	1.168325	1681.15	302.85	0.6078	297.40	1.177019	1710.84	290.27	0.6026
309.40	1.168502	1681.75	302.59	0.6077	297.15	1.177201	1711.45	290.02	0.6025
309.15	1.168680	1682.35	302.32	0.6076	296.90	1.177373	1712.06	289.77	0.6024
308.90	1.168859	1682.96	302.06	0.6075	296.65	1.177553	1712.67	289.52	0.6023
308.65	1.169036	1683.55	301.80	0.6074	296.40	1.177729	1713.28	289.27	0.6022
308.40	1.169213	1684.16	301.54	0.6073	296.15	1.177905	1713.90	289.01	0.6021
308.15	1.169391	1684.76	301.28	0.6072	295.90	1.178085	1714.52	288.76	0.6019
307.90	1.169567	1685.36	301.02	0.6071	295.65	1.178265	1715.13	288.51	0.6018
307.65	1.169742	1685.96	300.76	0.6070	295.40	1.178438	1715.75	288.26	0.6017
307.40	1.169922	1686.56	300.50	0.6069	295.15	1.178617	1716.36	288.01	0.6016
307.15	1.170102	1687.17	300.23	0.6068	294.90	1.178798	1716.97	287.76	0.6015
306.90	1.170276	1687.77	299.98	0.6067	294.65	1.178971	1717.58	287.52	0.6014
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306.40	1.170632	1688.98	299.45	0.6065	294.15	1.179325	1718.81	287.02	0.6012
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291.65	1.181104	1724.95	284.55	0.6000	279.40	1.189760	1755.38	272.77	0.5944
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290.40	1.181990	1728.05	283.32	0.5995	278.15	1.190632	1758.50	271.60	0.5938
290.15	1.182162	1728.67	283.07	0.5994					
289.90	1.182339	1729.29	282.83	0.5993					
289.65	1.182515	1729.91	282.58	0.5991					

289.39	1.182700	1730.84	282.24	0.5990
289.15	1.182877	1731.59	281.95	0.5989
288.89	1.183052	1732.13	281.73	0.5988
288.64	1.183228	1732.78	281.48	0.5987
288.39	1.183407	1733.34	281.25	0.5986
288.15	1.183574	1733.91	281.03	0.5985
287.90	1.183753	1734.51	280.79	0.5983
287.64	1.183941	1735.04	280.58	0.5982
287.40	1.184107	1735.67	280.33	0.5981
287.15	1.184289	1736.27	280.10	0.5980
286.90	1.184462	1736.82	279.88	0.5979
286.65	1.184637	1737.45	279.63	0.5978
286.40	1.184815	1738.07	279.39	0.5977
286.15	1.184986	1738.68	279.16	0.5975
285.90	1.185168	1739.24	278.93	0.5974
285.65	1.185344	1739.86	278.69	0.5973
285.40	1.185519	1740.47	278.46	0.5972
285.15	1.185700	1741.08	278.22	0.5971
284.90	1.185886	1741.82	277.94	0.5970
284.64	1.186059	1742.42	277.71	0.5968
284.40	1.186228	1742.99	277.49	0.5967
284.15	1.186403	1743.61	277.25	0.5966
283.90	1.186582	1744.21	277.02	0.5965
283.65	1.186756	1744.84	276.78	0.5964
283.40	1.186933	1745.46	276.54	0.5963
283.15	1.187110	1746.08	276.30	0.5961
282.90	1.187288	1746.70	276.06	0.5960
282.65	1.187467	1747.32	275.82	0.5959
282.40	1.187641	1747.95	275.59	0.5958
282.15	1.187817	1748.57	275.35	0.5957
281.90	1.187991	1749.20	275.11	0.5956
281.65	1.188172	1749.83	274.87	0.5954
281.40	1.188344	1750.39	274.66	0.5953
281.15	1.188523	1751.00	274.42	0.5952

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280.90	1.188699	1751.60	274.19	0.5951					
280.40	1.189050	1752.86	273.72	0.5948					
280.15	1.189231	1753.49	273.48	0.5947					
279.90	1.189407	1754.12	273.24	0.5946					
279.65	1.189580	1754.75	273.01	0.5945					
2-hydroxy ethylammonium pentanoate (2-HEAPE)									
T (K)	ρ (gcm^{-3})	u (ms^{-1})	$κ_S$ (TPa^{-1})	$10^3 \cdot α$ (K^{-1})	T (K)	ρ (gcm^{-3})	u (ms^{-1})	$κ_S$ (TPa^{-1})	$10^3 \cdot α$ (K^{-1})
338.15	1.020672	1468.15	454.54	-3.6736	307.90	1.039467	1558.18	396.24	-3.8607
337.90	1.020820	1468.77	454.09	-3.6729	307.65	1.039618	1558.99	395.77	-3.8646
337.65	1.020969	1469.46	453.60	-3.6723	307.40	1.039772	1559.78	395.31	-3.8684
337.40	1.021126	1470.18	453.08	-3.6716	307.15	1.039925	1560.61	394.83	-3.8723
337.15	1.021280	1470.87	452.59	-3.6710	306.90	1.040077	1561.44	394.35	-3.8763
336.90	1.021436	1471.58	452.09	-3.6705	306.65	1.040230	1562.25	393.89	-3.8803
336.65	1.021593	1472.29	451.58	-3.6700	306.40	1.040384	1563.08	393.41	-3.8843
336.40	1.021745	1473.00	451.08	-3.6695	306.15	1.040533	1563.89	392.94	-3.8883
336.15	1.021898	1473.73	450.56	-3.6690	305.90	1.040687	1564.73	392.47	-3.8924
335.65	1.022205	1475.12	449.58	-3.6683	305.40	1.040991	1566.38	391.52	-3.9007
335.40	1.022364	1475.83	449.08	-3.6679	305.15	1.041143	1567.19	391.06	-3.9050
335.15	1.022520	1476.54	448.58	-3.6677	304.90	1.041297	1568.03	390.59	-3.9092
334.90	1.022671	1477.24	448.09	-3.6674	304.65	1.041450	1568.87	390.11	-3.9135
334.65	1.022828	1477.95	447.59	-3.6672	304.40	1.041602	1569.72	389.63	-3.9178
334.40	1.022986	1478.66	447.09	-3.6670	304.15	1.041753	1570.56	389.16	-3.9222
334.15	1.023146	1479.37	446.59	-3.6669	303.90	1.041907	1571.39	388.69	-3.9266
333.90	1.023305	1480.07	446.10	-3.6668	303.65	1.042059	1572.25	388.21	-3.9310
333.65	1.023463	1480.78	445.60	-3.6667	303.40	1.042209	1573.09	387.74	-3.9355
333.40	1.023622	1481.49	445.11	-3.6667	303.15	1.042363	1573.94	387.26	-3.9400
333.15	1.023780	1482.20	444.61	-3.6667	302.90	1.042516	1574.79	386.79	-3.9445
332.90	1.023940	1482.92	444.11	-3.6667	302.65	1.042668	1575.65	386.31	-3.9491
332.65	1.024100	1483.63	443.62	-3.6668	302.40	1.042820	1576.51	385.83	-3.9537
332.40	1.024257	1484.34	443.12	-3.6669	302.15	1.042972	1577.39	385.34	-3.9584
332.15	1.024414	1485.06	442.63	-3.6671	301.90	1.043124	1578.23	384.88	-3.9631
331.90	1.024574	1485.77	442.13	-3.6673	301.65	1.043277	1579.11	384.39	-3.9678
331.65	1.024732	1486.48	441.64	-3.6675	301.40	1.043429	1579.97	383.92	-3.9726
331.40	1.024890	1487.19	441.15	-3.6678	301.15	1.043579	1580.82	383.45	-3.9774

331.15	1.025050	1487.90	440.66	-3.6681	300.90	1.043732	1581.71	382.96	-3.9822
330.90	1.025207	1488.62	440.17	-3.6684	300.65	1.043883	1582.58	382.49	-3.9871
330.65	1.025363	1489.35	439.67	-3.6688	300.40	1.044037	1583.48	382.00	-3.9920
330.40	1.025523	1490.05	439.19	-3.6692	300.15	1.044188	1584.38	381.51	-3.9970
330.15	1.025679	1490.79	438.69	-3.6697	299.90	1.044340	1585.27	381.02	-4.0020
329.90	1.025838	1491.51	438.20	-3.6702	299.65	1.044492	1586.16	380.54	-4.0070
329.65	1.025997	1492.23	437.71	-3.6707	299.40	1.044644	1587.08	380.04	-4.0121
329.15	1.026310	1493.70	436.71	-3.6719	298.90	1.044973	1588.87	379.07	-4.0224
328.90	1.026467	1494.41	436.23	-3.6726	298.65	1.045148	1589.78	378.57	-4.0275
328.65	1.026627	1495.14	435.74	-3.6732	298.40	1.045311	1590.70	378.07	-4.0328
327.90	1.027097	1497.32	434.27	-3.6755	297.65	1.045807	1593.44	376.60	-4.0487
327.65	1.027255	1498.06	433.77	-3.6764	297.40	1.045975	1594.39	376.09	-4.0540
327.40	1.027411	1498.78	433.29	-3.6772	297.15	1.046142	1595.32	375.59	-4.0594
327.15	1.027568	1499.51	432.80	-3.6781	296.90	1.046304	1596.24	375.10	-4.0649
326.90	1.027725	1500.24	432.32	-3.6791	296.65	1.046470	1597.18	374.60	-4.0704
326.65	1.027883	1500.98	431.82	-3.6801	296.40	1.046642	1598.12	374.10	-4.0759
326.40	1.028039	1501.70	431.34	-3.6811	296.15	1.046804	1599.08	373.59	-4.0814
326.15	1.028194	1502.44	430.85	-3.6821	295.90	1.046975	1600.00	373.10	-4.0870
325.90	1.028352	1503.16	430.38	-3.6832	295.65	1.047135	1600.95	372.60	-4.0927
325.65	1.028508	1503.88	429.90	-3.6844	295.40	1.047303	1601.93	372.08	-4.0983
325.40	1.028665	1504.64	429.40	-3.6855	295.15	1.047465	1602.89	371.58	-4.1041
325.15	1.028822	1505.36	428.92	-3.6868	294.90	1.047628	1603.86	371.07	-4.1098
324.90	1.028976	1506.11	428.43	-3.6880	294.65	1.047795	1604.81	370.58	-4.1156
324.65	1.029135	1506.84	427.95	-3.6893	294.40	1.047960	1605.78	370.07	-4.1214
324.40	1.029289	1507.58	427.47	-3.6906	294.15	1.048125	1606.77	369.56	-4.1273
324.15	1.029445	1508.32	426.98	-3.6920	293.90	1.048288	1607.74	369.05	-4.1332
323.90	1.029602	1509.05	426.50	-3.6934	293.65	1.048451	1608.73	368.54	-4.1391
323.65	1.029757	1509.79	426.02	-3.6948	293.40	1.048614	1609.75	368.02	-4.1451
323.15	1.030071	1511.28	425.05	-3.6978	292.90	1.048944	1611.75	366.99	-4.1571
322.90	1.030226	1512.02	424.57	-3.6993	292.65	1.049105	1612.77	366.47	-4.1632
322.65	1.030381	1512.75	424.10	-3.7009	292.40	1.049271	1613.76	365.96	-4.1693
322.40	1.030537	1513.50	423.62	-3.7025	292.15	1.049433	1614.77	365.45	-4.1755
322.15	1.030693	1514.23	423.14	-3.7042	291.90	1.049593	1615.76	364.94	-4.1817
321.90	1.030846	1514.98	422.66	-3.7059	291.65	1.049759	1616.79	364.42	-4.1879

321.65	1.031002	1515.72	422.18	-3.7076	291.40	1.049921	1617.83	363.90	-4.1942
321.40	1.031159	1516.46	421.71	-3.7094	291.15	1.050082	1618.87	363.37	-4.2005
321.15	1.031314	1517.21	421.23	-3.7112	290.90	1.050244	1619.95	362.83	-4.2068
320.90	1.031468	1517.96	420.75	-3.7130	290.65	1.050407	1620.99	362.31	-4.2132
320.65	1.031625	1518.71	420.27	-3.7149	290.40	1.050566	1622.02	361.80	-4.2196
320.40	1.031780	1519.46	419.79	-3.7168	290.15	1.050730	1623.16	361.23	-4.2261
320.15	1.031934	1520.22	419.31	-3.7188	289.90	1.050889	1624.19	360.72	-4.2326
319.90	1.032088	1520.97	418.83	-3.7208	289.65	1.051050	1625.29	360.18	-4.2391
319.65	1.032243	1521.73	418.35	-3.7228	289.40	1.051211	1626.38	359.64	-4.2457
319.40	1.032399	1522.49	417.87	-3.7249	289.15	1.051372	1627.47	359.10	-4.2523
319.15	1.032553	1523.24	417.40	-3.7270	288.90	1.051531	1628.60	358.55	-4.2590
318.90	1.032709	1524.00	416.92	-3.7292	288.65	1.051691	1629.70	358.01	-4.2656
318.65	1.032862	1524.77	416.44	-3.7313	288.40	1.051853	1630.82	357.46	-4.2724
318.40	1.033016	1525.53	415.96	-3.7336	288.15	1.052010	1631.92	356.93	-4.2791
318.15	1.033171	1526.28	415.49	-3.7358	287.90	1.052170	1633.05	356.38	-4.2859
317.90	1.033327	1527.05	415.01	-3.7381	287.65	1.052330	1634.18	355.83	-4.2928
317.40	1.033635	1528.57	414.06	-3.7428	287.15	1.052647	1636.52	354.71	-4.3065
317.15	1.033790	1529.33	413.59	-3.7452	286.90	1.052803	1637.66	354.16	-4.3135
316.65	1.034098	1530.86	412.64	-3.7502	286.40	1.053121	1639.97	353.06	-4.3275
316.40	1.034253	1531.63	412.16	-3.7527	286.15	1.053282	1641.17	352.49	-4.3345
316.15	1.034406	1532.39	411.69	-3.7552	285.90	1.053440	1642.36	351.93	-4.3416
315.90	1.034559	1533.16	411.22	-3.7578	285.65	1.053595	1643.59	351.35	-4.3488
315.40	1.034867	1534.71	410.26	-3.7631	285.15	1.053914	1645.91	350.25	-4.3632
315.15	1.035022	1535.47	409.80	-3.7659	284.90	1.054069	1647.20	349.65	-4.3704
314.90	1.035175	1536.22	409.34	-3.7686	284.65	1.054227	1648.38	349.10	-4.3777
314.65	1.035330	1536.99	408.86	-3.7714	284.40	1.054384	1649.68	348.50	-4.3850
314.40	1.035483	1537.77	408.39	-3.7742	284.15	1.054542	1650.96	347.91	-4.3924
314.15	1.035638	1538.53	407.92	-3.7771	283.90	1.054697	1652.23	347.32	-4.3998
313.90	1.035792	1539.30	407.46	-3.7800	283.65	1.054853	1653.49	346.74	-4.4072
313.65	1.035945	1540.06	406.99	-3.7829	283.40	1.055012	1654.78	346.15	-4.4147
313.40	1.036100	1540.83	406.53	-3.7859	283.15	1.055166	1656.17	345.52	-4.4222
313.15	1.036252	1541.60	406.06	-3.7889	282.90	1.055325	1657.46	344.93	-4.4297
312.90	1.036406	1542.37	405.60	-3.7919	282.65	1.055479	1658.73	344.35	-4.4373
312.65	1.036558	1543.14	405.13	-3.7950	282.40	1.055637	1660.17	343.70	-4.4449

312.40	1.036711	1543.91	404.67	-3.7981	282.15	1.055795	1661.49	343.10	-4.4526
312.15	1.036865	1544.69	404.20	-3.8013	281.90	1.055948	1662.83	342.50	-4.4603
311.90	1.037019	1545.47	403.73	-3.8045	281.65	1.056104	1664.24	341.87	-4.4680
311.65	1.037171	1546.25	403.26	-3.8077	281.40	1.056260	1665.61	341.26	-4.4758
311.40	1.037325	1547.02	402.80	-3.8110	281.15	1.056416	1667.01	340.63	-4.4836
311.15	1.037479	1547.82	402.33	-3.8143	280.90	1.056572	1668.41	340.01	-4.4914
310.65	1.037785	1549.39	401.39	-3.8210	280.40	1.056883	1671.29	338.74	-4.5072
310.40	1.037938	1550.17	400.93	-3.8244	280.15	1.057038	1672.76	338.10	-4.5152
310.15	1.038089	1550.96	400.46	-3.8279	279.90	1.057192	1674.21	337.46	-4.5232
309.90	1.038244	1551.75	400.00	-3.8314	279.65	1.057349	1675.59	336.86	-4.5312
309.65	1.038396	1552.56	399.52	-3.8349	279.40	1.057504	1677.18	336.17	-4.5393
309.40	1.038550	1553.36	399.05	-3.8385	279.15	1.057659	1678.69	335.52	-4.5474
309.15	1.038704	1554.16	398.58	-3.8421	278.90	1.057816	1680.20	334.86	-4.5556
308.90	1.038856	1554.95	398.12	-3.8458	278.65	1.057971	1681.62	334.25	-4.5637
308.65	1.039008	1555.77	397.64	-3.8494	278.40	1.058124	1683.11	333.61	-4.5720
308.40	1.039161	1556.55	397.18	-3.8532	278.15	1.058279	1684.75	332.91	-4.5802
308.15	1.039313	1557.36	396.71	-3.8569					

Table 2. Densities (ρ), ultrasonic velocity (u), isentropic compressibilities (κ_S), isobaric expansibilities (α), 278.15-338.15K

The contrary effect is observed for conductivity. At the same temperature, higher viscosity was observed when the salt was of higher molecular weight. The effect of the temperature is similar for all salts.

A frequently applied derived property for industrial mixtures is the isobaric expansibility or thermal expansion coefficient (α), expressed as the temperature dependence of density. Thermal expansion coefficients are calculated by means of $(-\Delta\rho/\rho)$ as a function of temperature and assuming that α remains constant in any thermal range. As in the case of pure chemicals it can be computed by way of the expression:

$$\alpha = -\left(\frac{\partial \ln\rho}{\partial T}\right)_{P,x} \tag{2}$$

taking into account the temperature dependence of density. The results gathered in Table 2 showed that a minimum of isobaric expansibility is obtained (in terms of negative values) at approximately the same temperature for all ILs. The smaller the size of the cation (monoethylene cation), the lower the value of isobaric expansibility was obtained.

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Temperature (K)	2-HEAF	2-HEAPE
278.15	2158.20	83.6
288.15	3069.00	143.3
298.15	4197.60	239.6
308.15	5623.20	453.4
318.15	6959.70	632.6
328.15	8563.50	910.8
338.15	10404.90	1202.9

Table 3. Values of ionic conductivity ($\mu S \bullet cm^{-1}$) of the 2-HEAF and 2-HEAPE in the range 278.15 – 338.15 K

The values of ionic conductivity are gathered in Table 3. These results show an increasing trend for higher temperatures in each case. This fact may be ascribed to the increasing mobility of the ions for increased temperatures. At the same time, the ionic conductivity values decrease when molecular weight increases, thus 2-HEAPE has a lower ionic conductivity than 2-HEAF, the shortest member of this IL family [23].

The factor studied in this work is the chain length of the anion. The influence of anion residue is higher in terms of steric hindrance, due to its longer structure [2, 23]. This factor produces a higher disturbation on ion package. This fact may be observed in terms of higher values of densities and ultrasonic velocities for those salts of the lighter anion [37].

The ILs studied in this work showed interesting properties for industrial use: low cost of preparation, simple synthesis and purification methods. Moreover, the very low toxicity and the degradability have been verified [38]. Thus, sustainable processes can be originated from their use.

With this in mind, we decided to test their catalytic potential for several aldol condensation reactions with interest for fine chemicals synthesis. At industrial level aldol condensations are catalyzed by homogeneous alkaline bases (KOH or NaOH) [39,40] but with this kind of catalysts numerous disadvantages arise such as loss of catalysts due to separation difficulties, corrosion problems in the equipment and generation of large amounts of residual effluents which must be subsequently treated to minimize their environmental impact. Consequently, new technological solutions have to be developed in order to generate new and more environmental friendly processes.

The condensation reaction between citral and acetone leads to the formation of pseudoionones which are precursors in the commercial production of vitamin A. In the last years, the aldol condensation between citral and acetone has been studied by several groups employing different types of catalysts: rehydrated hydrotalcites [41], mixed oxides derived from hydrotalcites [42, 43], organic molecules [44], ionic liquids [28] etc.

Using the mixed oxides derived from hydrotalcites Climent et al. [42, 43] obtained a conversion of 83% and selectivity to pseudoionones of 82% in 1 h. Abello et al. obtained a citral conversion of 81% in only 5 min employing rehydrated hydrotalcites as catalysts [41] highlighting that Brønsted basic sites are more active than Lewis sites for aldol condensation reactions. In the study of Cota et al. [44] it was shown that 1,8-diazabicyclo[5.4.0]undec-7-ene

(DBU) which has Lewis basic properties, is inactive for aldol condensation reactions; however when it reacts with equimolar amounts of water, this molecule transforms towards a complex that shows Brønsted basic properties and becomes active giving a conversion of 89.17% and a selectivity of 89.6% in 6 h. When choline hydroxide (ionic liquid) was used as catalyst a citral conversion of 93% and selectivity of 98.2% were obtained in 1 h [28].

Among the ILs studied in this work, for citral and acetone condensation (entry 1, Table 4) the most active IL is 2-HEAA, which gives a conversion of 52%, the less active is 2-HEAiB which gives a conversion of 10%. The selectivity obtained in this reaction ranges between 49-83%. No traces of diacetone alcohol derived from the self-condensation of acetone were found but other secondary products coming from the self-condensation of citral and oligomers derived from citral are detected in small quantities in the reaction mixture.

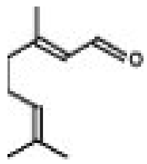
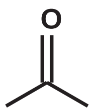
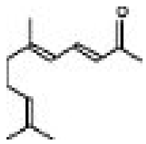
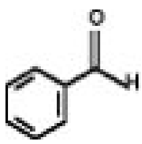
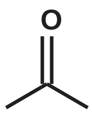
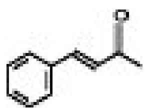
Entry	Substrate	Ketone	Product	Catalyst	Time	Conversion	Selectivity
					(h)	(%)	(%)
1				2-HEAF	7	35	83
				2-HEAP		40	63
				2-HEAA		52	74
				2-HEAB		33	60
				2-HEAiB		10	53
				2-HEAPE		38	49
2				2-HEAF	4	94	82
				2-HEAP	3	100	86
				2-HEAA	4	99	85
				2-HEAB	2	99	85
				2-HEAiB	2	93	85
				2-HEAPE	2	98	77

Table 4. Condensation reactions catalyzed by the studied ILs.

For the production of benzylideneacetone from the aldol condensation between acetone and benzaldehyde, Cota et al. [44] obtained a conversion of 99.9% and 93.97 selectivity in 2 h. When choline hydroxide was employed as catalyst [28] the total conversion was obtained in 0.1 hours but due to the production of dibenzylidenacetone the selectivity to benzylidenacetone decreased around 77%.

When ILs presented in this study were employed for this reaction (entry 2, Table 4), in 2 h of reaction, a conversion of 99% and a selectivity of 85% are obtained when using 2-HEAB as catalyst. Good conversion was also obtained with 2-HEAiB (93%) and 2-HEAPE (98%) with selectivity of 85% and 77% respectively. The decrease in the selectivity to benzylidenacetone is due to the formation of secondary products which include products of aldolisation of benzylidenacetone, like dibenzylidenacetone and other oligomers. The other studied ILs reached the maximum conversion in 3h (2-HEAP) and 4h (2-HEAF and 2-HEAA) and provided high selectivities between 82-86%.

For the repeated runs experiments, we used 2-HEAB in the condensation reaction between acetone and benzaldehyde. The catalyst was recycled 3 times, and in all runs a very good conversion was obtained. The results are presented in Figure 2.

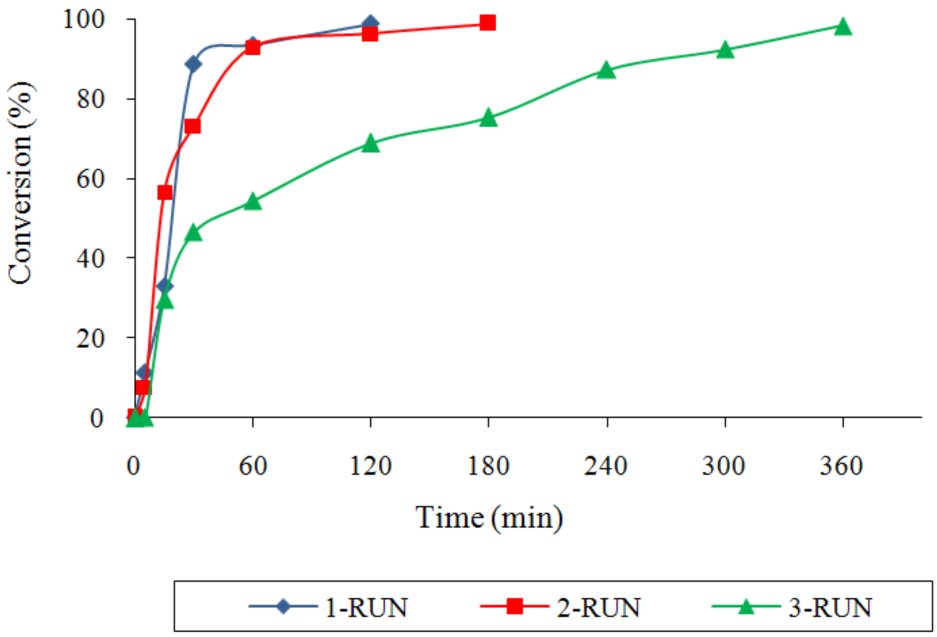


Figure 2. Repeated runs experiments using 2-HEAB in benzylideneacetone synthesis.

The loss of activity noticed in the second and third run can be attributed, on one hand to the loss of IL during the separation process and on the other hand due to the absorption of reaction products on the active sites of the catalyst. IL is partially soluble in the reaction product therefore during the separation procedure small quantities of IL can be dissolved in the organic phase and therefore lost during the separation process. This hypothesis is sustained by the evolution of the specific bands of the ILs which appear in the range 3500-2400 cm^{-1}, almost disappearing in the re-used sample as Figure 3 shows.

A weak band around 1591 cm^{-1} is present in the re-used sample accounting for the carbonyl stretching and N-H plane bending vibrations. On the other hand, deactivation of the catalyst, moreover exhibiting a dark yellow color, is probably due to the adsorption of oligomers and other secondary products on the surface of the catalyst during the reaction. This hypothesis is supported by the appearance of new bands in the re-used IL spectrum. The bands detected in the 1700-1200 cm^{-1} region corresponding to the symmetric and stretching vibrations of CH modes can be assigned to oligomeric species adsorbed on the surface. On the other hand in the 1260-700 cm^{-1} region bands which are normally weak appear and can be assigned to the C-C skeletal vibrations.

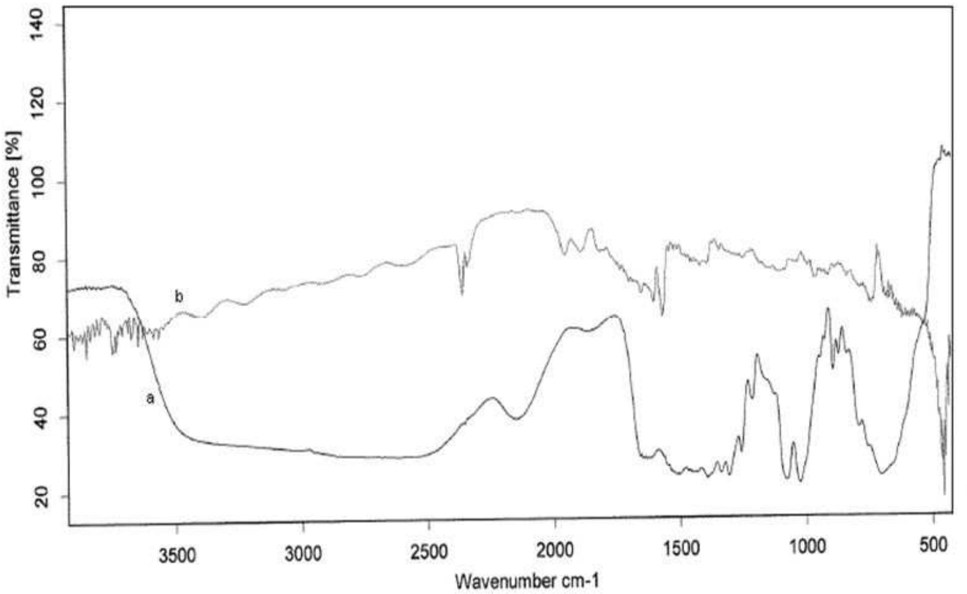


Figure 3. FT-IR spectra for (a) 2-HEAB before reaction, (b) 2-HEAB after reaction (3 consecutive runs).

In order to facilitate the recovery and re-use of the ILs we decided to immobilize them on a solid support. Immobilization and supporting of ILs can be achieved by simple impregnation, covalent linking of the cation or the anion, polymerization etc [45-47]. Compared to pure ILs, immobilized ILs facilitate the recovery and re-use of the catalyst. Previous reports describe the immobilization of ILs by adsorption or grafting onto silica surface and their use as catalysts for reactions like Friedel-Crafts acylation [45], hydrogenation [48] and hydroformilation [49]. Organic polymers [30], natural polymers [50] and zeolites [51] have been also used as supports for ILs.

For this purpose, the ILs were supported on alanine, a cheap readily available aminoacid. Their catalytic activity was tested in the same reactions as the pure ILs.

The catalytic activity results of the a-ILs for the citral-acetone condensation are presented in Table 5. After 6 h of reaction, the two isomers of citral can be converted into the corresponding pseudoionone with conversion between 30-56% except for a-HEAiB for which a conversion of 9% was obtained. The most active IL for this reaction is a-2-HEAA which provides a conversion of 56%. The selectivity obtained in this reaction ranges between 48-80%. No traces of diacetone alcohol derived from the self-condensation of acetone were found, but other secondary products coming from the self condensation of citral and oligomers derived from citral are detected in the reaction mixture. The support (entry 1) is not catalytically active.

In the condensation reaction of benzaldehyde and acetone the first step is the deprotonation of an acetone molecule to give the enolate anion whose nucleophilic attack on the C=O group of benzaldehyde leads to the β-aldol. This latter is easily dehydrated on weak acid sites and benzylidenacetone is obtained.

Entry	Catalyst	Conversion	Selectivity
		(%)	(%)
1	alanine	0	0
2	a-2-HEAF	30	61
3	a-2-HEAA	56	74
4	a-2-HEAP	49	80
5	a-2-HEAB	35	63
6	a-2-HEAiB	9	52
7	a-2-HEAPE	33	48

Table 5. Conversion at 6 h for citral-acetone condensation catalyzed by a-ILs

Entry	Catalyst	Conversion	Selectivity
		(%)	(%)
1	alanine	0	0
2	a-2-HEAF	99	83
3	a-2-HEAA	99	82
4	a-2-HEAP	99	85
5	a-2-HEAB	99	84
6	a-2-HEAiB	78	82
7	a-2-HEAPE	98	80

Table 6. Conversion at 2 h for benzaldehyde-acetone condensation catalyzed by a-ILs

In 2 hours of reaction a conversion of 98-99% is achieved for the majority of a-ILs, while a lower conversion (78%) is obtained for a-2-HEAiB (Table 6). The selectivity toward benzylidenacetone is around 80-86% due to the formation of dibenzylidenacetone as secondary product. The support, alanine (entry 1) is not active for citral acetone condensation.

It is noteworthy that, for both studied reactions, the conversions obtained with the a-ILs are in the same range as the ones obtained with free ILs (Figure 4 and 5).

The a-ILs are easily separated from the reaction mixture and reused. For the consecutive runs experiments we chose condensation between benzaldehyde and acetone as model reaction. The catalysts were recycled for 3 consecutive runs and in all runs a very good conversion was obtained. The results are presented in Figure 6.

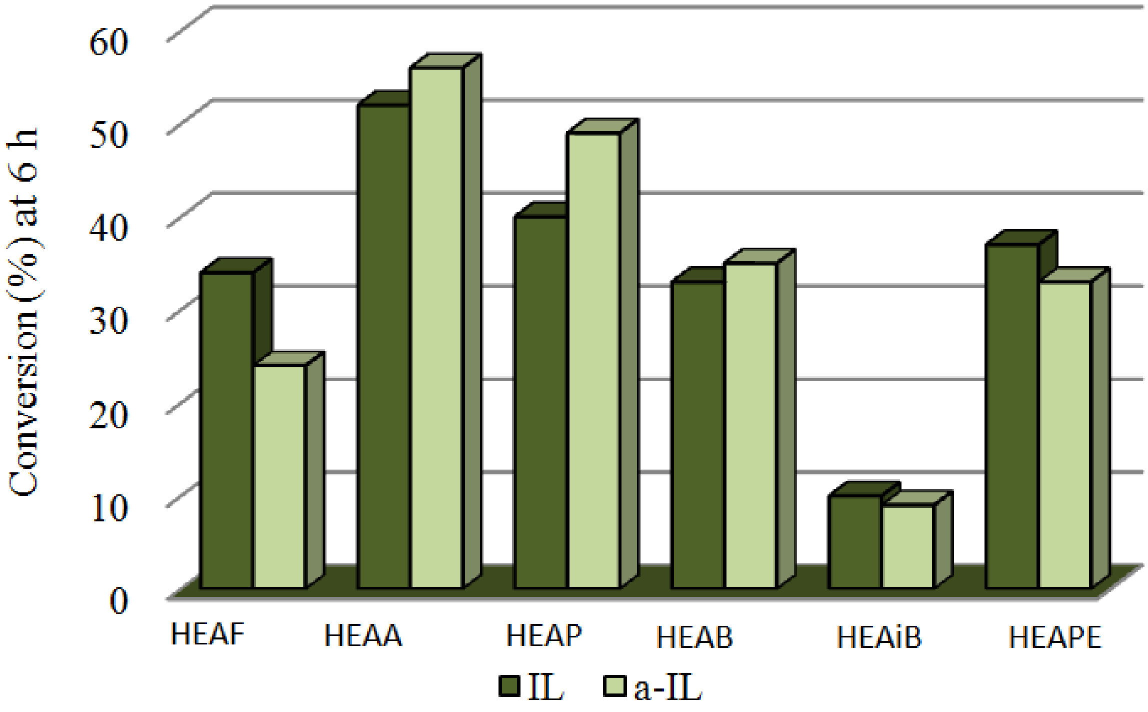


Figure 4. Conversion at 6 h for citral-acetone condensation for free ILs and a-ILs.

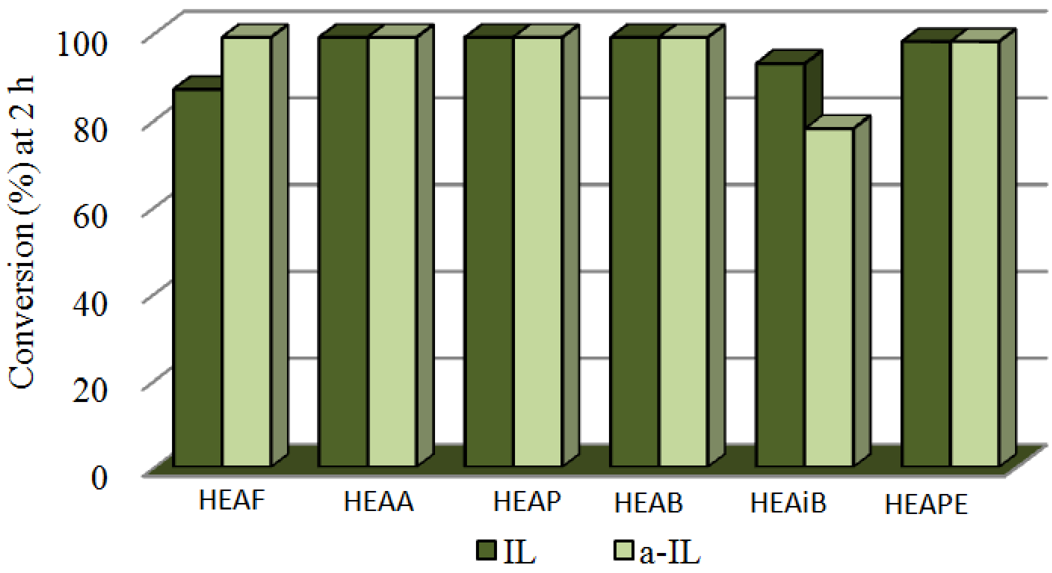


Figure 5. Conversion at 2 h for benzaldehyde-acetone condensation for free ILs and a-ILs.

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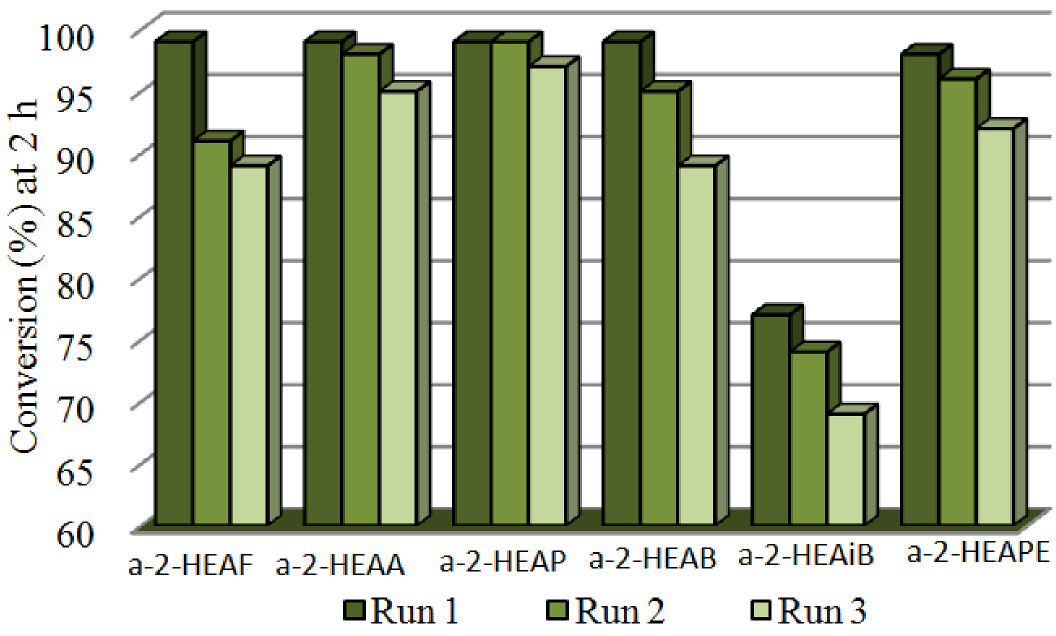

Figure 6. Consecutive runs experiments in benzaldehyde acetone condensation.

In the case of each IL, only a negligible loss of activity is detected in the second and third run which can be attributed to the possible adsorption of reactants or reaction products to the active sites of the catalyst.

From the comparison made with the aforementioned basic catalysts employed for these two aldol condensation reactions we can conclude that the ILs presented in this study are not the most active catalysts for these reactions but due to their green character and easy separation from the reaction media represent a convenient and environmental friendly alternative for the traditional homogeneous catalysts.

4. Conclusions

In this work, we present a simple and efficient synthesis protocol for protic ionic liquids and the experimental data for density, ultrasonic velocity and ionic conductivity of these liquid salts. It was found that increased temperature diminishes the interaction among ions and therefore lower values of density, ultrasonic velocity, viscosity, surface tension and refractive index are obtained for increased temperatures in each case. The contrary effect is observed for conductivity.

The influence of chain length of the anion on the physicochemical properties of the ILs has been also studied. The effect of the anion residue is higher in terms of steric hindrance, due to its longer structure. This factor produces a higher disturbation on ion package. The physicochemical data of ILs are important for both, designing cleaner technological processes and understanding the interactions in this kind of compounds

The catalytic potential of these new ILs was tested for two aldol condensation reactions with interest for fine chemistry industry. Conversions ranging from 35 to 52% and selectivities up to 83% are obtained for the condensation of citral with acetone. In the synthesis of benzilidenacetone, conversions above 93% with selectivities around 85% are obtained. We also studied the optimization of the recovery process of the ILs and their reuse in repeated runs of experiments. The catalysts can be recycled and reused for three consecutive cycles without significant loss of activity.

In addition, in order to improve the recovery process, the ILs were immobilized on alanine, a cheap readily available aminoacid. The catalytic activity of the alanine supported ILs was tested for citral-acetone and benzaldyde-acetone condensations. It is noteworthy that, for both studied reactions, the conversions obtained with the a-ILs are in the same range as the ones obtained with free ILs; moreover the catalysts can be recycled and reused for three consecutive cycles without significant loss of activity.

The ILs studied in this work showed interesting properties for industrial use: low cost of preparation, simple synthesis and purification methods. Moreover, the very low toxicity and the degradability have been verified. Thus, sustainable processes can be originated from their use.

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