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# New Brønsted Ionic Liquids: Synthesis, Thermodynamics 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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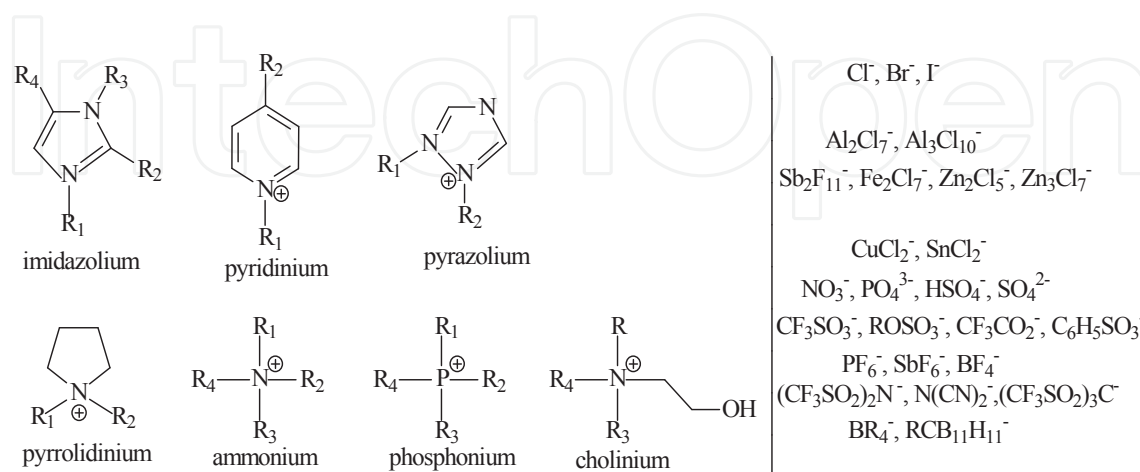
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## 1. Introduction

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 reactions [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°C; 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<sub>N</sub>2 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<sub>2</sub>/SO<sub>2</sub> 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  $\text{RNH}_3^+$  combined with organic anions of the form  $\text{R}'\text{COO}^-$  (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:



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

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<sup>-3</sup> and 1 m s<sup>-1</sup>. 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 0.01  $\mu$ S to 1 mS and accuracy of  $\pm 0.5\%$  at the range temperature. The accuracy of temperature into the measurement cell was  $\pm 0.5$  °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  $\times$  0.32 mm  $\times$  0.25  $\mu$ m). 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<sub>2</sub>O 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<sup>-1</sup> 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<sup>-1</sup> 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.

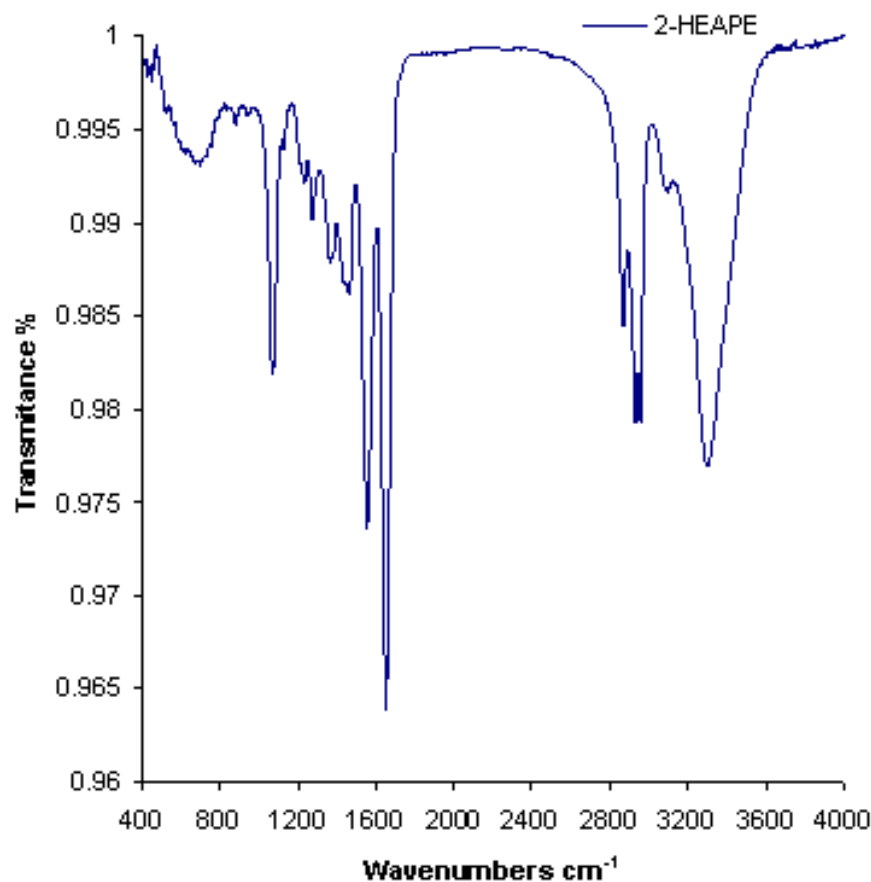


Figure 1. FT-IR spectrum for 2-HEAPE.

| IL      | Molecular Weight<br>(g•mol <sup>-1</sup> ) | Exp. Density<br>(g•cm <sup>-3</sup> ) | Exp. Ultrasonic Velocity<br>(ms <sup>-1</sup> ) | Exp. Conductivity<br>(μS•cm <sup>-1</sup> ) |
|---------|--|---------------------------------------|---|---|
| 2-HEAF  | 107.11                                     | 1.176489                              | 1709.00   | 4197.6                                      |
| 2-HEAPE | 163.21                                     | 1.045479                              | 1591.59   | 239.6                                       |

<sup>a</sup>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<sup>a</sup>

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.



| 2-hydroxy ethylammonium formate (2-HEAF) |                                |                          |                                    |   |          |                                |                          |                                    |   |
|--|--------------------------------|--------------------------|------------------------------------|---|----------|--------------------------------|--------------------------|------------------------------------|---|
| T<br>(K)                                 | $\rho$<br>(gcm <sup>-3</sup> ) | u<br>(ms <sup>-1</sup> ) | $\kappa_s$<br>(TPa <sup>-1</sup> ) | $10^3 \cdot \alpha$<br>(K <sup>-1</sup> ) | T<br>(K) | $\rho$<br>(gcm <sup>-3</sup> ) | u<br>(ms <sup>-1</sup> ) | $\kappa_s$<br>(TPa <sup>-1</sup> ) | $10^3 \cdot \alpha$<br>(K <sup>-1</sup> ) |
| 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 |
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| 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 |
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| 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 |

|        |          |         |        |        |        |          |         |        |        |
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| 310.40 | 1.167794 | 1679.35 | 303.63 | 0.6081 | 298.15 | 1.176489 | 1709.00 | 291.02 | 0.6029 |
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| 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 |
| 306.65 | 1.170454 | 1688.37 | 299.72 | 0.6066 | 294.40 | 1.179148 | 1718.20 | 287.27 | 0.6013 |
| 306.40 | 1.170632 | 1688.98 | 299.45 | 0.6065 | 294.15 | 1.179325 | 1718.81 | 287.02 | 0.6012 |
| 306.15 | 1.170810 | 1689.58 | 299.20 | 0.6064 | 293.90 | 1.179505 | 1719.42 | 286.77 | 0.6011 |
| 305.90 | 1.170986 | 1690.18 | 298.94 | 0.6063 | 293.65 | 1.179682 | 1720.04 | 286.52 | 0.6009 |
| 305.65 | 1.171165 | 1690.79 | 298.68 | 0.6062 | 293.40 | 1.179858 | 1720.66 | 286.27 | 0.6008 |
| 305.40 | 1.171343 | 1691.39 | 298.42 | 0.6060 | 293.15 | 1.180037 | 1721.27 | 286.03 | 0.6007 |
| 305.15 | 1.171518 | 1691.99 | 298.16 | 0.6059 | 292.90 | 1.180210 | 1721.88 | 285.78 | 0.6006 |
| 304.90 | 1.171699 | 1692.60 | 297.90 | 0.6058 | 292.65 | 1.180390 | 1722.50 | 285.53 | 0.6005 |
| 304.40 | 1.172053 | 1693.80 | 297.39 | 0.6056 | 292.15 | 1.180744 | 1723.72 | 285.04 | 0.6003 |
| 304.15 | 1.172230 | 1694.41 | 297.13 | 0.6055 | 291.90 | 1.180923 | 1724.34 | 284.80 | 0.6002 |
| 291.65 | 1.181104 | 1724.95 | 284.55 | 0.6000 | 279.40 | 1.189760 | 1755.38 | 272.77 | 0.5944 |
| 291.40 | 1.181278 | 1725.57 | 284.30 | 0.5999 | 279.15 | 1.189935 | 1756.03 | 272.53 | 0.5943 |
| 291.15 | 1.181453 | 1726.18 | 284.06 | 0.5998 | 278.90 | 1.190108 | 1756.62 | 272.31 | 0.5941 |
| 290.90 | 1.181631 | 1726.80 | 283.81 | 0.5997 | 278.65 | 1.190288 | 1757.23 | 272.08 | 0.5940 |
| 290.65 | 1.181809 | 1727.43 | 283.56 | 0.5996 | 278.40 | 1.190464 | 1757.88 | 271.83 | 0.5939 |
| 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 |

|        |          |         |        |        |
|--------|----------|---------|--------|--------|
| 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<br>(K) | $\rho$<br>(gcm <sup>-3</sup> ) | $u$<br>(ms <sup>-1</sup> ) | $\kappa_s$<br>(TPa <sup>-1</sup> ) | $10^3 \cdot \alpha$<br>(K <sup>-1</sup> ) | T<br>(K) | $\rho$<br>(gcm <sup>-3</sup> ) | $u$<br>(ms <sup>-1</sup> ) | $\kappa_s$<br>(TPa <sup>-1</sup> ) | $10^3 \cdot \alpha$<br>(K <sup>-1</sup> ) |
|----------|--------------------------------|----------------------------|------------------------------------|---|----------|--------------------------------|----------------------------|------------------------------------|---|
| 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 ( $\rho$ ), ultrasonic velocity ( $u$ ), isentropic compressibilities ( $\kappa_s$ ), isobaric expansibilities ( $\alpha$ ), 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 ( $\alpha$ ), 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  $\alpha$  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 (mono-ethylene cation), the lower the value of isobaric expansibility was obtained.



| 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 ( $\mu\text{S}\cdot\text{cm}^{-1}$ ) 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 disturbance 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.

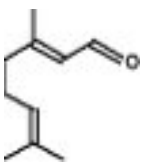
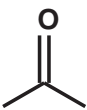
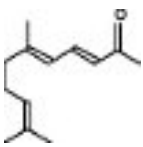
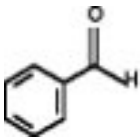
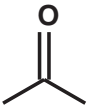
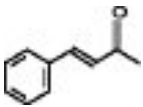
With this in mind, we decided to test their catalytic potential for several aldol condensation reactions with interest for fine chemicals synthesis. At industrial level aldol condensations are catalyzed by homogeneous alkaline bases (KOH or NaOH) [39,40] but with this kind of catalysts numerous disadvantages 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.

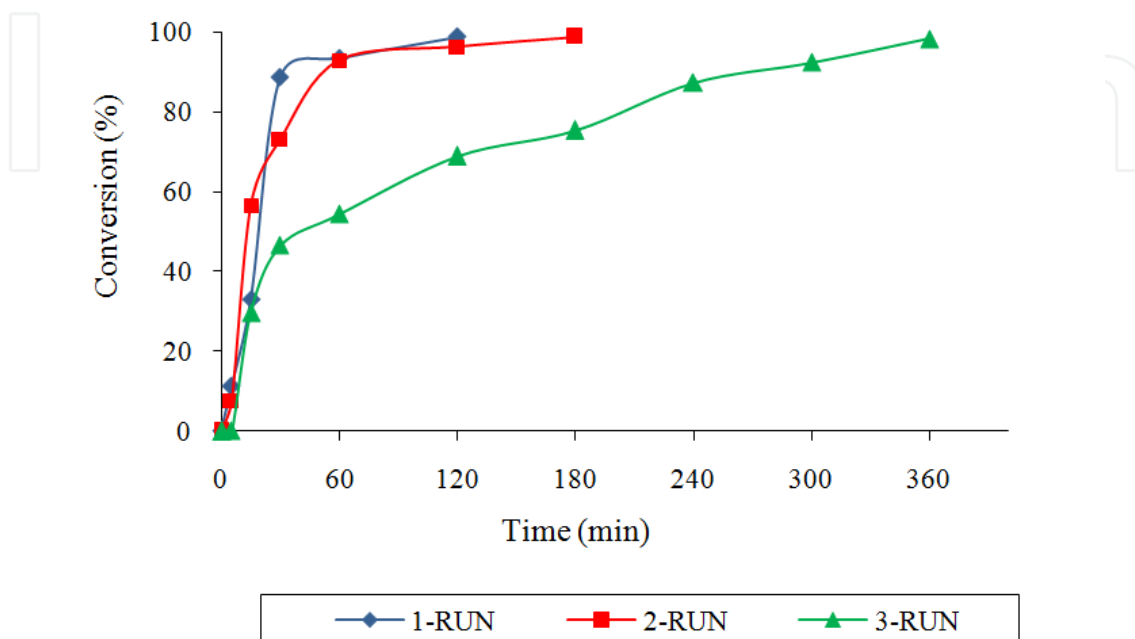
| Entry | Substrate   | Ketone  | Product   | Catalyst | Time<br>(h) | Conversion<br>(%) | Selectivity<br>(%) |
|-------|---|---|---|----------|-------------|-------------------|--------------------|
| 1     |   |    |    | 2-HEAF   | 7           | 35                | 83                 |
|       |   |   |   | 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 benzylidenacetone 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%.

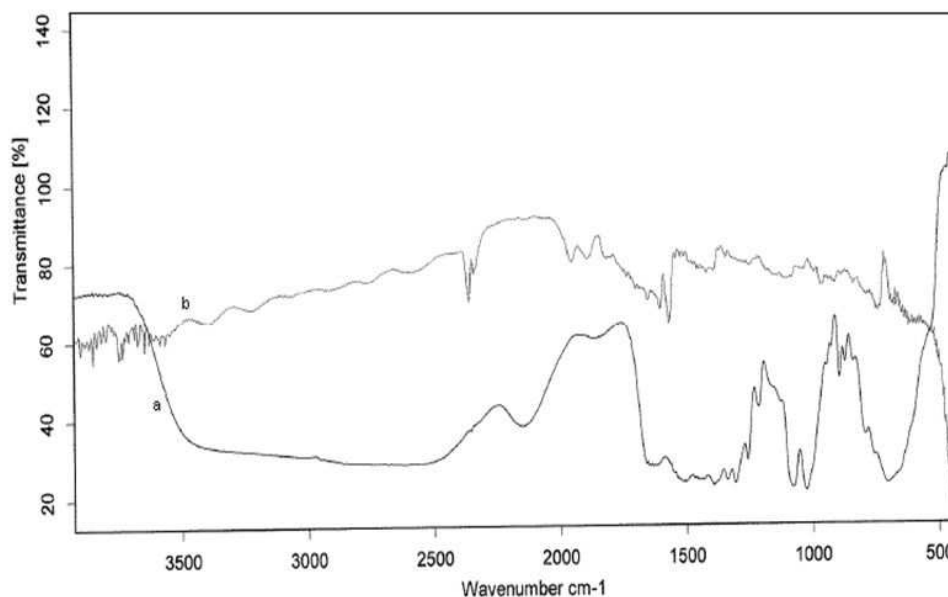
For the repeated runs experiments, we used 2-HEAB in the condensation reaction between acetone and benzaldehyde. The catalyst was recycled 3 times, and in all runs a very good conversion was obtained. The results are presented in Figure 2.



**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  $3500\text{--}2400\text{ cm}^{-1}$ , almost disappearing in the re-used sample as Figure 3 shows.

A weak band around  $1591\text{ cm}^{-1}$  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  $1700\text{--}1200\text{ cm}^{-1}$  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  $1260\text{--}700\text{ cm}^{-1}$  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 hydroformylation [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 amino acid. 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  $\beta$ -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 benzyli-  
denacetone 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 reac-  
tion. The catalysts were recycled for 3 consecutive runs and in all runs a very good conver-  
sion was obtained. The results are presented in Figure 6.

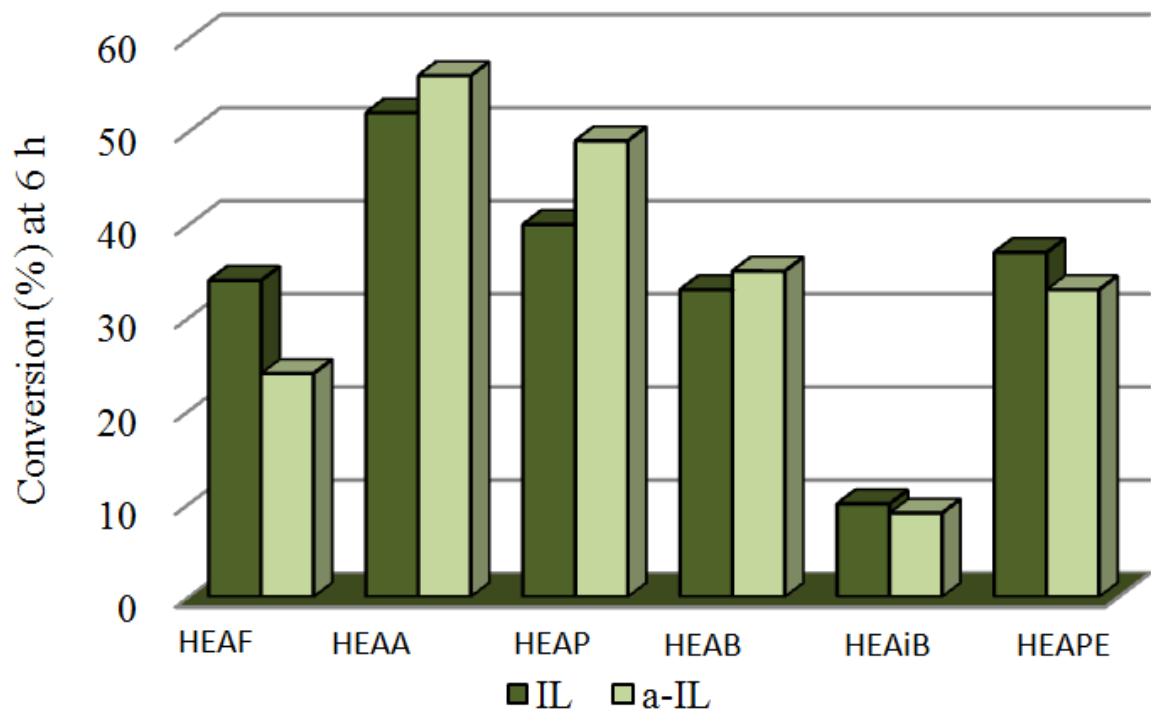


Figure 4. Conversion at 6 h for citral-acetone condensation for free ILs and a-ILs.

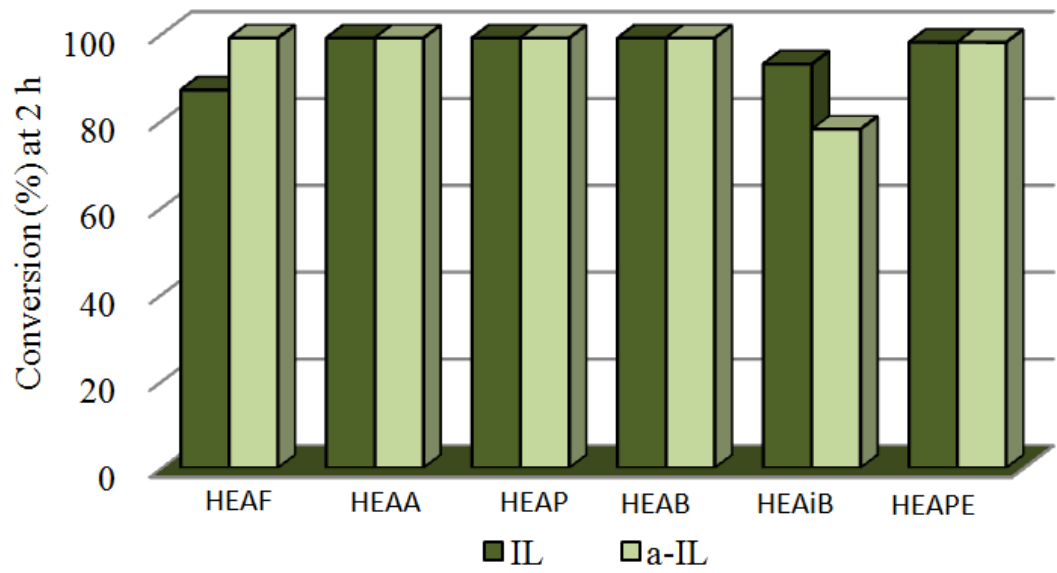
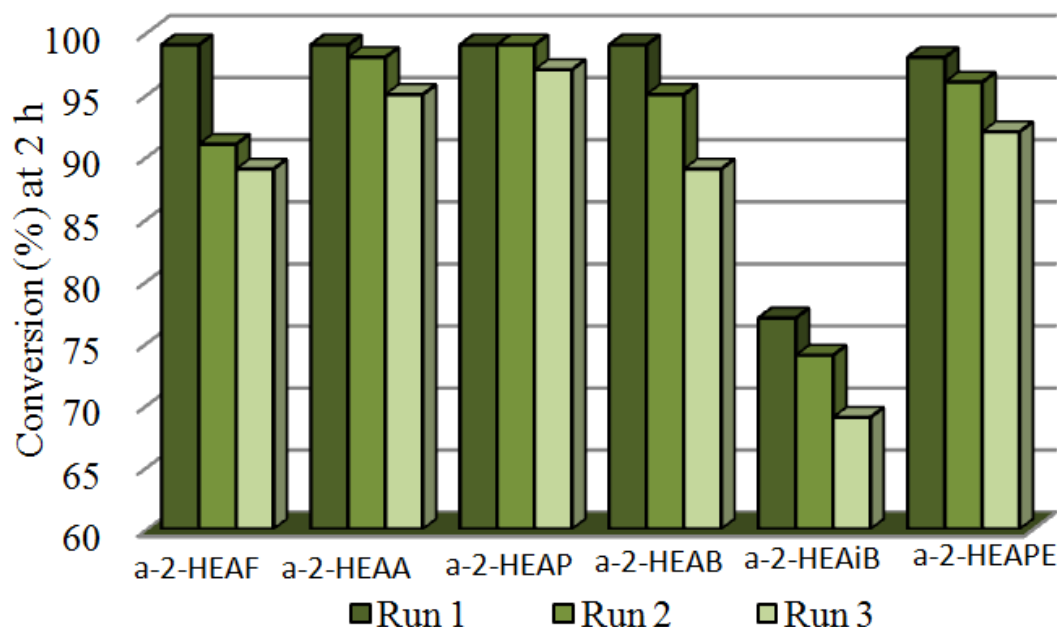


Figure 5. Conversion at 2 h for benzaldehyde-acetone condensation for free ILs and a-ILs.



**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 disturbance on ion package. The physi-



cochemical 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 benzilide-nacetone, 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 benzaldehyde-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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