



## Brønsted ionic liquids: Study of physico-chemical properties and catalytic activity in aldol condensations

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### ABSTRACT

A serie of substituted amines based ionic liquids was prepared using an aliphatic linear carboxylic acid (pentanoic acid). The ionic liquids synthesised are 2-hydroxy ethylammonium pentanoate (2-HEAPE), 2-hydroxy diethylammonium pentanoate (2-HDEAPE) and 2-hydroxy triethylammonium pentanoate (2-HTEAPE). FT-IR spectra establishes their ionic salt structure. The influence of structural variations on their thermodynamic properties (density, ultrasonic velocity, ionic conductivity, refractive index, viscosity and surface tension) was investigated, as a function of temperature in the range 278.15–338.15 K. In the compounds studied here, the anion has strong effect on the properties if compared with previous studies of the authors, when shorter chains were used. It was found that the elongation of the alkyl chain causes the pronounced depression of fluidity and ionic conductivity. The observed temperature trend of the studied properties points out the special packing of these ionic liquids, as well as, the strong influence of the steric hindrance among linear aliphatic residues. We also describe the catalytic activity of these type of ionic liquids for a representative serie of aldol condensation processes. Conversions higher than 98% and selectivities higher than 85% were obtained. Moreover the catalysts are easily separated from reaction mixture and re-used, obtaining good conversions for at least three consecutive cycles. As a conclusion, it was found that simple structural modifications into anion length and degree of substitution provide a mechanism to manipulate the catalytic potency of these ionic liquids, as well as, tailor physico-chemical properties for potential end-use applications.

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### 1. Introduction

Ionic liquids (ILs) are a class of new solvents which are increasingly being used in a wide variety of applications in the last years due to an amazing number of desirable properties [1–4]. Their field of potential study is growing at a very fast rate, as their beneficial properties are identified and then applied into processes. ILs are defined as those ionic salts which have a melting point below 100 °C and are formed by positive and negative ions. Typically, these compounds have excellent chemical and thermal stability, negligible vapour pressure and many of them are described as environmental friendly. They provide an attractive alternative to traditional nonionic organic solvents in a wide spectrum of applications and therefore, are considered highly promising neoteric solvents. ILs

can be divided into two broad categories: aprotic ionic liquids (AILs) and protic ionic liquids (PILs). The later are produced through proton transfer from a Brønsted acid to a Brønsted base. The former have received greater attention, nevertheless, recently there has been an increasing interest in PILs or Brønsted ILs due to their potential as environmental friendly solvents and promising applications [5–7].

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 develop of lesser harmful compounds as ILs. In the past few years, room-temperature ILs have found numerous applications as clean solvents and catalysts for green chemistry, in photochemistry, in electrosynthesis [8–12] and other applications as lubricants, electrolytes for batteries, new procedures for cheaper solar cells or cleaning applications in processes of minimization of CO<sub>2</sub>/SO<sub>2</sub> emissions [13–18].

With this fact in mind, and as a continuation of a wider project to develop and study applications of new ILs, in this work we present the study of physico-chemical properties and the catalytic

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potential of a new family of PILs. These PILs consist of substituted amine cations of the form  $R_XNH$  ( $X$  is the number of alkyl substitutions) combined with organic anions of the form  $R'COO^-$  (being of different nature  $R$  and  $R'$ ). These kind of compounds have low cost of preparation and simple synthesis/purification [5–7]. Moreover, the very low toxicity and the degradability of this kind of ILs has been verified [19]. Thus, sustainable processes can be originated with their use. The variations in the anion alkyl chain, in conjunction with different cations, lead to a large matrix of ILs.

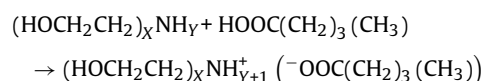
In order to obtain information related to internal organization, density, ultrasonic velocity, ionic conductivity, refractive index, viscosity and surface tension, were measured in a wide range of temperature for the following PILs: 2-hydroxy ethylammonium pentanoate (2-HEAPE), 2-hydroxy diethylammonium pentanoate (2-HDEAPE) and 2-hydroxy triethylammonium pentanoate (2-HTEAPE). As far as we know, open literature does not show publications related with these new PILs, therefore no information is available about their thermodynamic data, phase behaviour, mixing trend or temperature dependence until now.

We also describe the catalytic activity and recycling of 9 different PILs of the same family into a serie of aldol condensation processes. Our work is now being oriented towards phase studies of ILs, industrial applications related to separation and energy and heterogeneous catalysis.

## 2. Experimental

### 2.1. Preparation of the ILs

The amine compounds (monoethanolamine, diethanolamine or triethanolamine, Merck Synthesis, purity higher than 99%) were placed in a threenecked 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 and strong agitation are necessary to increase miscibility between reactants and then allow reaction. The organic acid (pentanoic acid, Merck Synthesis, purity higher than 99%) was added dropwise 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 (purification step explained below) or was stored at freezing temperature for a few months after synthesis. The reaction is an acid–base neutralization creating a pentanoate salt of mono, di or tri ethanolamine, that in a general form should be expressed as follows:



where  $X$  is the number of ethanol substitutions into the amine compound and  $Y$  is the protons ( $X + Y = 3$ ). For example, when  $X = 1$  and  $Y = 2$ , this equation shows the chemical reaction for the reactants monoethanolamine + pentanoic acid, and 2-hydroxy ethylammonium pentanoate (2-HEAPE) as neutralization product.

### 2.2. Stability at room-temperature

For many of these fused ammonium salts, exists the possibility to undergo a condensation reaction and form an amide compound. Therefore, an adequate control of temperature is essential during the chemical reaction of salt formation, otherwise heat evolution may produce the dehydration of the salt to give the corresponding amide as in the case of nylon salts (salts of diamines with dicarboxy acids). As observed in our laboratory during IL synthesis, dehydra-

tion starts around 423 K, for the lightest ILs from this family. The colour varies in each case from transparent to dark brown when reaction process and purification (strong agitation and slight heating for vaporization of residual non-reacted acid at least for 72 h) was 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.

### 2.3. Spectroscopy test

FT-IR spectrum was taken by a Jasco FT/IR 680 plus model IR spectrometer, using a NaCl disk. As Fig. 1 shows, the broad band in the  $3500\text{--}2400\text{ cm}^{-1}$  range exhibits characteristic ammonium structure for all the neutralization products. The OH stretching vibration is embedded in this band. The broad band centered at  $1600\text{ cm}^{-1}$  is a combined band of the carbonyl stretching and N–H plane bending vibrations.

### 2.4. 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 [5]. The molar mass and experimental results at standard condition for the ILs are shown in Table 1.

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  $10^{-5}\text{ g cm}^{-3}$  and  $1\text{ m s}^{-1}$ . 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  $\pm 10^{-2}\text{ K}$  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  $0.01\text{ }\mu\text{S}$  to  $1\text{ mS}$  and accuracy of  $\pm 0.5\%$  at the range temperature. The accuracy of temperature into the measurement cell was  $\pm 0.5\text{ }^\circ\text{C}$ .

The kinematic viscosity ( $\nu$ ) was determined from the transit time of the liquid meniscus through a capillary viscosimeter supplied by Schott (Cap No. 0c,  $0.46\text{ (}0.01\text{ mm internal diameter, }K\text{) }0.003201\text{ mm}^2\text{ s}^{-1}$ ) measured with an uncertainty of  $(0.00008\text{ mm}^2\text{ s}^{-1})$  using Eq. (1):

$$\nu = K(t - \theta) \quad (1)$$

where  $t$  is the efflux time,  $K$  is the characteristic constant of the capillary viscosimeter, and  $\theta$  is a correction value to prevent the final effects. An electronic stopwatch accurate within  $\pm 0.01\text{ s}$  was used for measuring efflux times. The capillary viscosimeter was immersed in a bath controlled to  $\pm 0.1\text{ }^\circ\text{C}$ . The viscosimeter was a Shott-Geräte AVS 350 Ubbelohde viscosimeter. Each measurement was repeated at least 10 times. The dynamic viscosity ( $\eta$ ) was obtained by the product of kinematic viscosity ( $\nu$ ) and the corresponding density ( $\rho$ ) of the mixture in terms of Eq. (2) for each temperature and mixture composition.

$$\eta = \rho \cdot \nu \quad (2)$$

The surface tensions of the mixtures were measured using a Kruss K-9 tensiometer, which employs the Wilhelmy plate principle. The surface tensions of the pure components were determined and compared with literature values to calibrate the tensiometer.

The uncertainty of the measurement was  $\pm 0.03 \text{ mN m}^{-1}$ . In general, each surface tension value reported was an average of five measurements. The samples were thermostated in a closed vessel before surface tension measurements to prevent evaporation.

Refractive index was determined to within  $\pm 1 \times 10^{-6}$  using an Atago RX-1000 refractometer. Before measurements, the refractometer was calibrated using distilled–deionized water in accordance with the instrument instructions. Water was circulated into the instrument through a thermostatically controlled bath maintained constant to  $\pm 0.1^\circ \text{C}$ . The samples were directly injected from the stock solution stored at working temperature to avoid evaporation. The refractive index measurements were done after the liquid samples reached the constant temperature of the refractometer. The detailed experimental procedure has been described into previous works of the authors [5–7].

### 2.5. Catalytic studies

Recently, many studies [20–25] dealing with the application of ILs in organic synthesis and catalysis have been published, pointing out the vast interest in this type of compounds. With these facts in mind, we studied the catalytic potential of the serie of ILs gathered before and 6 ILs belonging to the same compounds family [26].

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 ( $15 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu\text{m}$ ). 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  $\text{H}_2\text{O}$  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

### 3.1. Thermodynamic properties

The variation with the temperature of different thermodynamic properties measured in this work are gathered in Figs. 2–8. These figures show an increasing trend in the packing efficiency of the ILs as the molecular weight increases.

This tendency shows a continuous decrease of the density and ultrasonic velocity versus temperature in each case (Figs. 2 and 3). 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:

$$\alpha = - \left( \frac{\partial \ln \rho}{\partial T} \right)_{P,x} \quad (5)$$

taking into account the temperature dependence of density. These  $\alpha$  values showed a minimum (in terms of negative values) for each case at 333.41 K (Fig. 4).

In Fig. 5, the ionic conductivity of the ILs is depicted, and it can be observed 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 the cation's ramification increases. So the influence of molecular structure, in terms of conductivity, produces the lowest values for 2-HTEAPE and the highest for 2-HEAPE, but all of them have a lower ionic conductivity than 2-hydroxy ethylammonium formate (2-HEAF) (the shortest member of this IL family) [6].

In Figs. 6–8, the variation with the temperature of the refraction, viscosity and surface tension are depicted. In each case, it can be observed a decreasing tendency for increasing temperatures and molar weight decrease.

The ions enclosed in this study are of two types: linear the anion and linear (mono), plane (di) or globular (trisubstitution) the cation. The factors studied here are the chain length of the anion (comparatively with earlier results of the authors) and the substitution into the cation (bulk degree), respectively. The influence of anion residue is higher in terms of steric hindrance, due to its longer structure [6,7]. This factor produces a higher disturbance on ion package. For these ions, the bulk cation develops a lower steric hindrance influence than the anion. Ion's mobility and progressively higher kinetics, make more and more difficult the ion–ion interaction and then weaker structures into liquid phase.

For compact and smooth representation, the measured properties of the ILs were correlated as a function of temperature in accordance to the Eq. (S1). Eq. (S1), fitting parameters and the values for Figs. 2–8. are found in supplementary material.

### 3.2. Catalytic activity

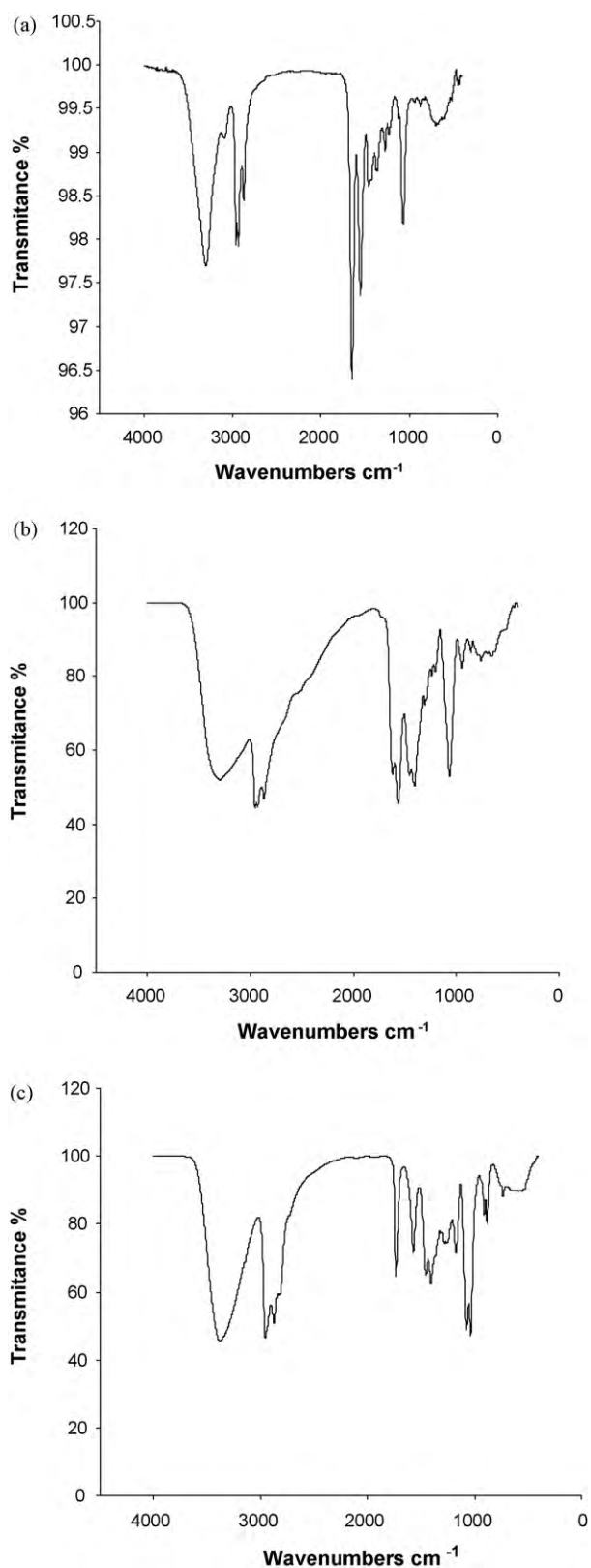
In the present work the studied ILs were 2-hydroxi (mono, di or tri) ethylammonium butanoate (2-HEAB, 2-HDEAB and 2-HTEAB, respectively), 2-hydroxi (mono, di or tri) ethylammonium isobutanoate (2-HEAiB, 2-HDEAiB and 2-HTEAiB, respectively) and 2-hydroxi (mono, di or tri) ethylammonium pentanoate (2-HEAPE, 2-HDEAPE, and 2-HTEAPE, respectively). The synthesis and characterization of these ILs of butanoate and isobutanoate anions were presented earlier [26].

At industrial level aldol condensations are catalyzed by homogeneous alkaline bases (KOH or NaOH) [27,28] 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.

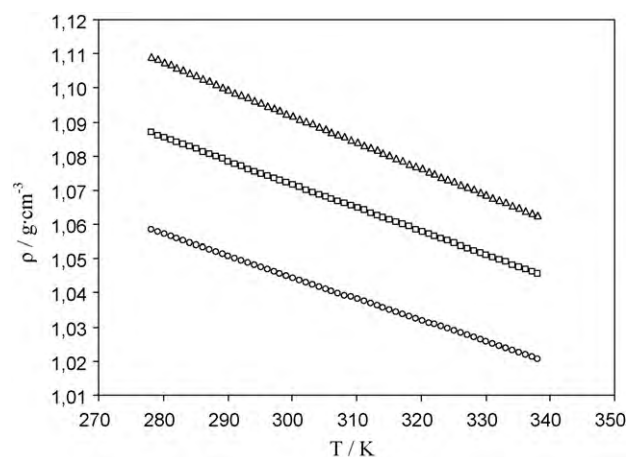
**Table 1**

Experimental data for pure ILs at 298.15 K and other relevant information (other experimental data for comparison are not available from open literature).

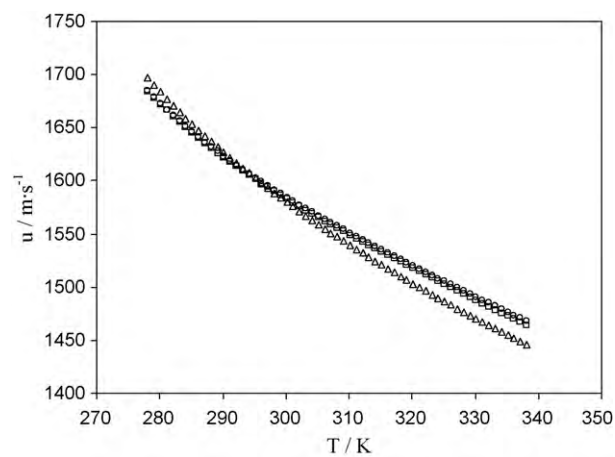
ILs	Molecular weight (Mw, g mol <sup>-1</sup> )	Exp. density ( $\rho$ , g cm <sup>-3</sup> )	Exp. ultrasonic velocity ( $u$ , m s <sup>-1</sup> )	Exp. conductivity (C, $\mu\text{S cm}^{-1}$ )	Exp. refractive index ( $n_D$ )	Exp. dynamic viscosity ( $\mu$ , mPa s <sup>-1</sup> )	Exp. surface tension ( $\sigma$ , mN m <sup>-1</sup> )
2-HEAPE	163.21	1.045479	1591.59	239.6	1.46290	1270.1	34.32
2-HDEAPE	207.27	1.072811	1590.19	218.8	1.46854	803.2	34.09
2-HTEAPE	251.32	1.093275	1588.71	160.1	1.46893	505.5	33.37



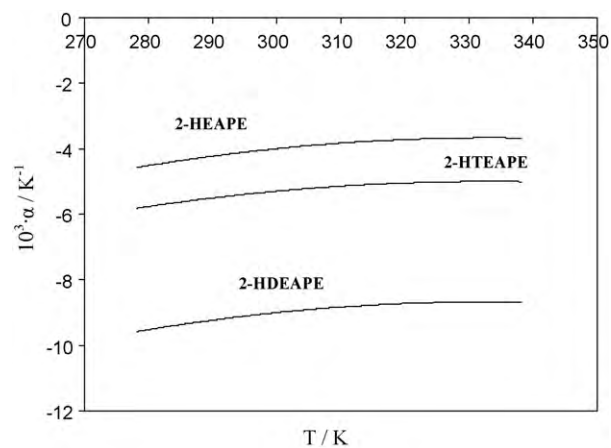
**Fig. 1.** FT-IR spectra for (a) 2-hydroxy ethylammonium propionate (2-HEAPE), (b) 2-hydroxy diethylammonium propionate (2-HDEAPE) and (c) 2-hydroxy triethylammonium propionate (2-HTEAPE).



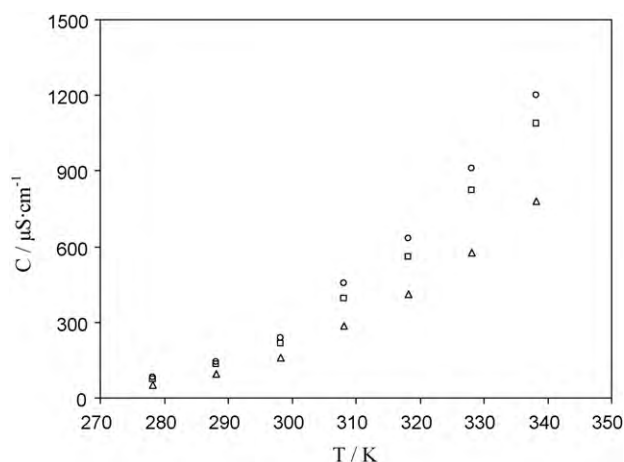
**Fig. 2.** Curves of density ( $\text{g cm}^{-3}$ ) for the studied ILs in the temperature range 278.15–338.15 K (( $\circ$ ) 2-hydroxy ethylammonium propionate (2-HEAPE), ( $\square$ ) 2-hydroxy diethylammonium propionate (2-HDEAPE) and ( $\triangle$ ) 2-hydroxy triethylammonium propionate (2-HTEAPE)).



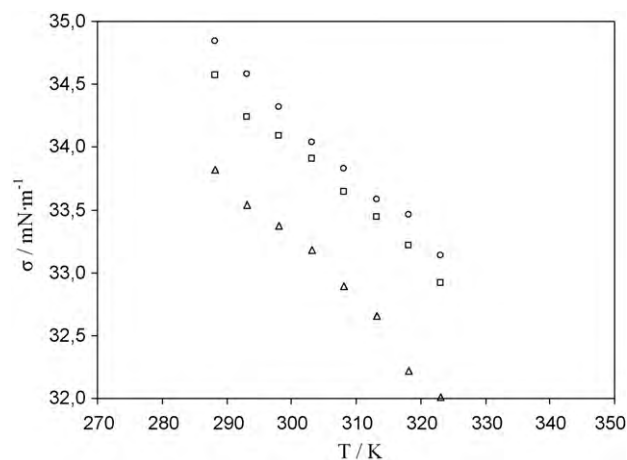
**Fig. 3.** Curves of ultrasonic velocity ( $\text{m s}^{-1}$ ) for the studied ILs in the temperature range 278.15–338.15 K (( $\circ$ ) 2-hydroxy ethylammonium propionate (2-HEAPE), ( $\square$ ) 2-hydroxy diethylammonium propionate (2-HDEAPE) and ( $\triangle$ ) 2-hydroxy triethylammonium propionate (2-HTEAPE)).



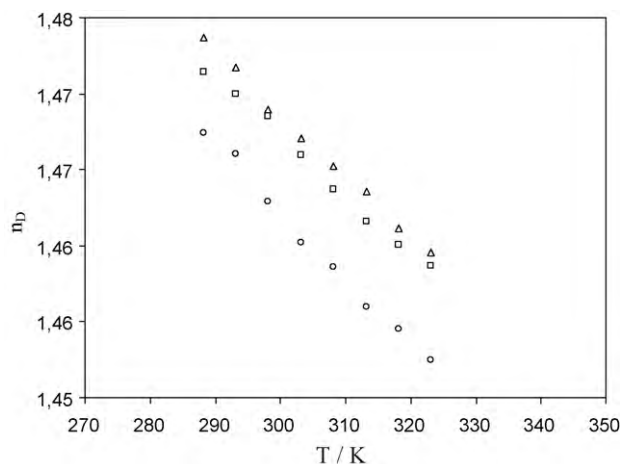
**Fig. 4.** Curves of isobaric expansibility ( $\text{K}^{-1}$ ) for the studied ILs in the temperature range 278.15–338.15 K.



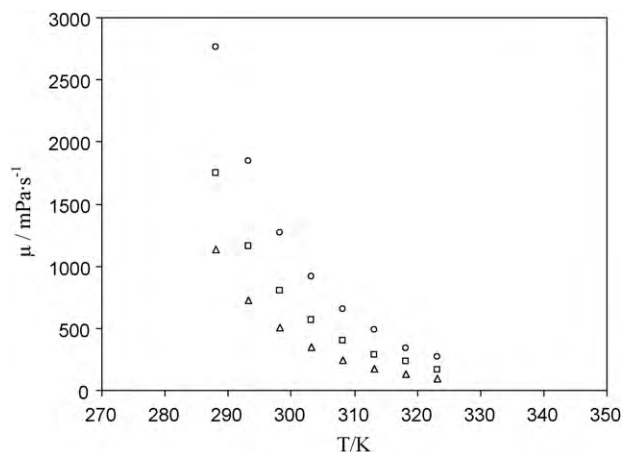
**Fig. 5.** Curves of ionic conductivity ( $\mu\text{S cm}^{-1}$ ) for the studied ILs in the temperature range 278.15–338.15 K (( $\circ$ ) 2-hydroxy ethylammonium propionate (2-HEAPE), ( $\square$ ) 2-hydroxy diethylammonium propionate (2-HDEAPE) and ( $\triangle$ ) 2-hydroxy triethylammonium propionate (2-HTEAPE)).



**Fig. 8.** Curves of surface tension ( $\text{mN m}^{-1}$ ) for the studied ILs in the temperature range 278.15–338.15 K (( $\circ$ ) 2-hydroxy ethylammonium propionate (2-HEAPE), ( $\square$ ) 2-hydroxy diethylammonium propionate (2-HDEAPE) and ( $\triangle$ ) 2-hydroxy triethylammonium propionate (2-HTEAPE)).



**Fig. 6.** Curves of refractive index for the studied ILs in the temperature range 278.15–338.15 K (( $\circ$ ) 2-hydroxy ethylammonium propionate (2-HEAPE), ( $\square$ ) 2-hydroxy diethylammonium propionate (2-HDEAPE) and ( $\triangle$ ) 2-hydroxy triethylammonium propionate (2-HTEAPE)).



**Fig. 7.** Curves of dynamic viscosities ( $\text{mPa s}^{-1}$ ) for the studied ILs in the temperature range 278.15–338.15 K (( $\circ$ ) 2-hydroxy ethylammonium propionate (2-HEAPE), ( $\square$ ) 2-hydroxy diethylammonium propionate (2-HDEAPE) and ( $\triangle$ ) 2-hydroxy triethylammonium propionate (2-HTEAPE)).

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 [29], mixed oxides derived from hydrotalcites [30,31], organic molecules [32], ionic liquids [25], etc.

Using the mixed oxides derived from hydrotalcites Climent et al. [30,31] 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 [29] highlighting that Brønsted basic sites are more active than Lewis sites for aldol condensation reactions. In the study of Cota et al. [32] 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 [25] in 1 h.

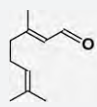

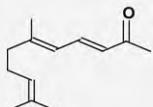
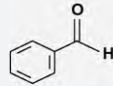

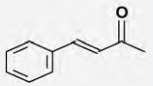
Among the ILs studied in this work, for citral and acetone condensation (entry 1, Table 2) the most active IL is 2-HEAPE, which gives a conversion of 37.6%, the less active is 2-HEAiB which gives a conversion of 10.4% while 2-HEAB gives an intermediate conversion of 33.2%. The selectivity obtained in this reaction ranges between 49.5 and 59.7%. 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.

For the production of benzylideneacetone from the aldol condensation between acetone and benzaldehyde, Cota et al. [32] obtained a conversion of 99.9% and 93.97% selectivity in 2 h. When choline hydroxide was employed as catalyst [25] the total conversion was obtained in 0.1 h but due to the production of dibenzylideneacetone the selectivity to benzylideneacetone decreased around 77%.

When ILs presented in this study were employed for this reaction (entry 2, Table 2) after 2 h of reaction a conversion of 98.8% and a selectivity of 85.6% are obtained when using 2-HEAB as catalyst. Good conversion was also obtained with 2-HEAiB (93.1%) and 2-HEAPE (98.4%) with selectivity of 85.3% and 77.2%, respectively. The decrease in the selectivity to benzylideneacetone is due to the formation of secondary products which include products of aldoli-

**Table 2**

Condensation reactions catalyzed by the studied ILs.

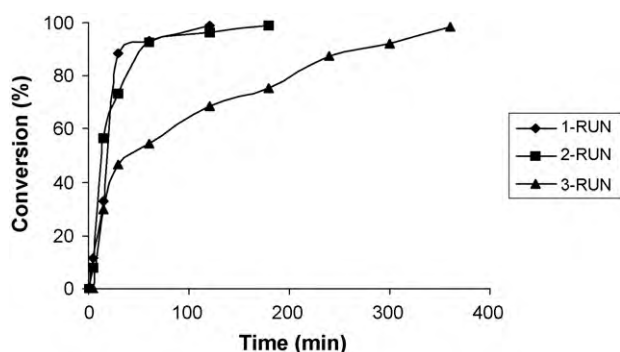
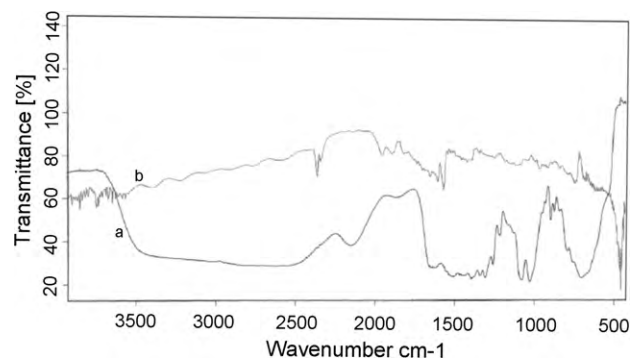
Entry	Substrate	Ketone	Product	Catalyst	Time (h)	Conversion (%)	Selectivity (%)
1				2-HEAB	7	33.2	59.7
				2-HEAiB		10.4	53.4
				2-HEAPE		37.6	49.5
2				2-HEAB	2	98.8	85.6
				2-HEAiB		93.1	85.3
				2-HEAPE		98.4	77.2

sation of benzylideneacetone, like dibenzylideneacetone and other oligomers.

The di- and tri-substituted ILs (2-HDEAB, 2-HTEAB, 2-HDEAiB, 2-HTEAiB, 2-HDEAPE, 2-HTEAPE) gave low conversions for the studied reactions. This low catalytic activity can be explained by the inaccessibility of the active sites of the catalyst due to the steric impediments produced by the ramification of the cation.

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.

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 Fig. 9. 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 Fig. 10 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 colour, 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

**Fig. 9.** Repeated runs experiments using 2-HEAB in benzylideneacetone synthesis.**Fig. 10.** FT-IR spectra for (a) 2-HEAB before reaction, (b) 2-HEAB after reaction (3 consecutive runs).

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.

#### 4. Conclusions

The physico-chemical data of ILs are important for both, designing cleaner technological processes and understanding the interactions in this kind of compounds. In the present paper, we present a novel synthesis protocol for a new family of protic ionic liquids. The ionic structure was determined by FT-IR. An extensive study containing experimental data for density, ultrasonic velocity, ionic conductivity, viscosity, surface tension and refractive index of the liquid salts 2-hydroxy ethylammonium pentanoate (2-HEAPE), 2-hydroxy diethylammonium pentanoate (2-HDEAPE) and 2-hydroxy triethylammonium pentanoate (2-HTEAPE) is also presented.

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 organic residual chain into both ions forming the IL has strong effects on the physico-chemical properties, being the steric hindrance a key factor for accommodation into a liquid structure.

The catalytic potential of this new ILs was tested for two aldol condensation reactions; good results in terms of conversion and selectivity were obtained. Moreover an efficient recovery process was developed, the catalysts being recycled and re-used for three consecutive cycles without significant loss of activity.

Based on these experimental observations and as explained above, because of the low cost and simplicity of synthesis, the potential interest of these liquid salts is amazing for industrial applications, as unit operations or cosolvents for catalytic reactions.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2010.06.008.

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