# New Short Aliphatic Chain Ionic Liquids: Synthesis, Physical Properties, and Catalytic Activity in Aldol Condensations

**I. Cota, R. Gonzalez-Olmos, M. Iglesias, and F. Medina***

*Departament d'Enginyeria Química, Escola Tècnica Superior d'Enginyeria Química, Universitat Rovira i Virgili, Avinguda Països Catalans 26, Campus Sescelades, 43007 Tarragona, España*

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This paper reports on the synthesis of new short aliphatic chain ionic liquids and the study of the temperature dependence of density, ultrasonic velocities, and ionic conductivity in the range of 278.15−338.15 K. Fourier transform infrared spectra establishes their simple ionic salt structure. Because of their polarity, the ionic liquids are able to dissolve polar solvents and inorganic salts, all of them showing high tolerance in hydroxylic media. 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 enclosed in anions and cations. One of them showed a very high melting temperature. A collection of slightly basic ionic liquids were used to test their catalytic activity in several aldol condensation reactions of some carbonyl compounds. The best conversions and selectivities were obtained using single ionic liquids, with no synergetic effects being observed when different concentrations of mixed ionic liquids were used as catalysts. In any case, the ionic liquid can also easily be recycled from reaction media, suggesting a promising method of process design for this kind of reaction.

## Introduction

Ionic liquids are versatile new media for many chemical synthesis, enzymatic catalysis, and green engineering processes.[1] They can be of hydrophobic or hydrophilic nature depending on the structures of ions. In fact, the ionic liquids consist solely of a collection of positive and negative ions. However, unlike conventional molten salts, these materials often melt at low temperatures. This is achieved because of the incorporation of bulky functional structures such as anions and/or cations and the fact that the structure prevents the ions from packing easily into an ordered electrostatic net structure and then a solid phase at ambient conditions. Ionic liquids can be used as solvents because of their low melting point, and, because of their ionic structure, when ionic liquids are used as solvents, better selectivity is obtained when compared with that of other conventional organic solvents. In the past few years, room-temperature ionic liquids have been also used as clean solvents and catalysts for green chemistry, as electrolytes for batteries, in photochemistry, and in electrosynthesis. Their potential interest rises from the necessities of cleaner processes and stronger environmental policies that will be applied. They have no significant vapor pressure and thus create no volatile organic pollution during manipulation of industrial operation. They also allow an easy separation of organic molecules by direct distillation without loss of the ionic liquid. Their liquid range can be as large as 300 °C, allowing for large reaction kinetic control, which, coupled with their good solvent properties, allows minimization of reactor design. Salts based upon poor nucleophilic anions such as $[BF_4]^-$, $[PF_6]^-$, $[CF_3CO_2]^-$, $[CF_3SO_3]^-$, and so forth, are insensitive to water and air and possess remarkably high thermal stability. Until now, many of these materials have been based on the imidazolium cation and, in a lesser proportion, alkyl pyridiniums and trialkylamines. By changing the anion or the alkyl chain of the cation, a wide variation in properties such as hydrophobicity, viscosity, density and solvation power can be obtained and then a tailored-made ionic liquid may be designed for specific industrial applications. Although many studies have been performed concerning their thermodynamics, little is yet known about the possibilities of new structures (so-called ionic liquid chemical families), as well as mixing ionic liquids thermodynamics. In what is referred to as reaction media, in the past few years, ionic liquids have been the subject of considerable interest in the context of green synthesis because of their wide acceptability as alternative reaction media[2,3] and have been found to act as selective catalysts for different reactions.

With this fact in mind, and as a continuation of a wider project to develop and study the applications of new ionic liquids,[4,5] the first part of the present work deals with the synthesis, Fourier transform infrared (FT-IR) identification, and thermodynamic characterization of different components of a new family of ionic liquids based on short organic chain acid and base (substituted amine) neutralization. This kind of compounds show interesting properties for the industrial use of ionic liquids: low cost of preparation and simple synthesis and purification methods. Additionally, in order to obtain information related to internal organization (and data of industrial interest), density, ultrasonic velocity, and ionic conductivity were measured in a wide range of temperature (278.15−338.15 K). In this paper, we have studied the synthesis and characterization of 2-hydroxy ethylammonium formate (2-HEAF), 2-hydroxy diethylammonium formate (2-HDEAF), and 2-hydroxy triethylammonium formate (2-HTEAF). As far as we know, the literature does not contain publications related to these new ionic liquids except for 2-HEAF, which was synthesized by Bicak,[6] and, moreover, no information about their thermodynamic characterization, phase behavior, mixing trend, or temperature dependence has been

* To whom correspondence should be addressed. Fax: +34 977559621. E-mail: francesc.medina@urv.cat.

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available until now. The observed inverse dependence on temperature of the density and ultrasonic velocity for these ionic liquids points out the special trend of packing and the strong dependence on ion kinetics. The rising values of ionic conductivity versus temperature may also be ascribed to faster mobility of the ions. The observed values are surprisingly lower than expected because of the strong influence of the steric hindrance of aliphatic residues into ions during the mixing process. For 2-HDEAF, only the range 323.15−338.15 K was studied because of its high melting point.

On the other hand, 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.[7] In the commercial production processes of the selected aldol condensations, NaOH and KOH are used as homogeneous catalysts;[8] however, this kind of catalyst has numerous disadvantages such as loss of catalyst due to the separation difficulties, corrosion problems in the equipment, and generation of large amounts of residues. Recently, because of the industrial importance of the process, there has been an interest in substituting conventional bases in the homogeneous phase by heterogeneous catalysts such as alkali oxides, basic alumina, and calcined[9] hydrotalcites. Ionic liquids have attracted growing interest in catalysis because of their physical and chemical properties. Recently, a new basic catalyst based on an ionic liquid (choline hydroxide) was described.[7] In this study, we describe the catalytic activity of a new family of ionic liquids, which is characterized by a short aliphatic chain structure for the anion and different substitution for the cation. The studied ionic liquids in terms of catalytic effect were 2-HEAF, 2-HDEAF, 2-HTEAF, 2-hydroxy ethylammonium acetate (2-HEAA), 2-hydroxy diethylammonium acetate (2-HDEAA), 2-hydroxy triethylammonium acetate (2-HTEAA), 2-hydroxy ethylammonium propionate (2-HEAP), 2-hydroxy diethylammonium propionate (2-HDEAP), and 2-hydroxy triethylammonium propionate (2-HTEAP). Because of the high melting point of 2-HTEAF, it was not possible to develop an experimental study. Those ionic liquids not included in this paper have been studied earlier.[5]

In order to determine the catalytic activity of the ionic liquids, several condensation reactions of some carbonyl compounds were carried out. The products obtained from these reactions have been applied in the pharmacological, flavor, and fragrance industries.

## Experimental Section

**Materials and Equipment.** During the course of the experiments, the purity of the ionic liquids was monitored by density and ultrasonic velocity measurements. The pure ionic liquids were stored in sunlight-protected form, in constant humidity, and at low temperature. The manipulation and purification techniques usually used in our experimental works were applied.[10] The molar mass and experimental results at standard conditions for the ionic liquids 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 $10^{-5}$ g cm$^{-3}$ and 1 m s$^{-1}$. Apparatus calibration was performed periodically in accordance with vendor instructions using a double reference (Millipore quality water and ambient air at each temperature). The accuracy in the measurement of temperature was better than $\pm 10^{-2}$ K by means of a temperature control device that applied the Peltier principle to maintain isothermal conditions during the measurements.

**TABLE 1: Experimental Data for Pure Ionic Liquids at 298.15 K and Other Relevant Information**[a]

| | molecular weight (g mol$^{-1}$) | exp. density (g cm$^{-3}$) | exp. ultrasonic velocity (m s$^{-1}$) | exp. conductivity ($\mu$S cm$^{-1}$) |
|---|---|---|---|---|
| 2-HEAF | 107.11 | 1.176489 | 1709.00 | 4197.6 |
| 2-HDEAF | 157.17 | 1.194041 | 1798.54 | 973.17 |
| 2-HTEAF[b] | 195.22 | 1.221864 | 1884.60 | 1843.38 |

[a] Other experimental data for comparison are not available from the literature. [b] 323.15 K.

The ion conductivity was measured by a Jenway model 4150 conductivity/TDS meter with a resolution of 0.01 $\mu$S to 1 mS and an accuracy of ±0.5% within the temperature range. The accuracy of the temperature of the measurement cell was ±0.5 °C.

**Preparation of the Ionic Liquids.** The amine compounds (monoethanolamine, diethanolamine, or triethanolamine, Merck Synthesis, better than 99%) were placed in a three-necked flask made entirely of 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 the miscibility between the reactants, and then the mixture is allowed to react. The formic acid (Merck Synthesis, better than 99%) was added dropwise to the flask under stirring with a magnetic bar. Stirring was continued for 24 h at the laboratory temperature, in order to obtain a final viscous liquid. Lower viscosity was observed in the final product by decreasing the molecular weight of the reactants. No solid crystals or precipitation was noticed when the liquid sample was purified or stored at freezing temperature for a few months after synthesis. The reaction is a simple acid−base neutralization creating an acetate or propionate salt of mono-, di- or triethanolamine, that, in a general form, should be expressed as follows:

$$(HOCH_2CH_2)_xNH_y + HOOCH \rightarrow (HOCH_2CH_2)_xNH^+_{y+1}(^-OOCH)$$

where $x$ is the number of ethanol substitutions into the amine compound, and $y$ is the number of protons ($x + y = 3$). For example, when $x = 1$ and $y = 2$, this equation shows the chemical reaction for the reactants monoethanolamine + formic acid, with 2-HEAF as the 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 ionic liquid synthesis, dehydration begins around 423.15 K for the lightest ionic liquids. 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 nonreacted acid for at least for 24 h) were completed. 2-HTEAF shows a solid phase at room temperature, having a melting point of 321.15 K; for this reason, thermodynamical studies were carried out at 323.15−338.15 K for this ionic liquid.

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

**TABLE 2: Densities ($\rho$), Ultrasonic Velocity ($u$), Isentropic Compressibilities ($\kappa_S$), and Isobaric Expansibilities ($\alpha$) at 278.15−338.15 K**

| $T$ (K) | $\rho$ (g cm$^{-3}$) | $u$ (m s$^{-1}$) | $\kappa_S$ (T Pa$^{-1}$) | $10^3 \cdot \alpha$ (K$^{-1}$) | $T$ (K) | $\rho$ (g cm$^{-3}$) | $u$ (m s$^{-1}$) | $\kappa_S$ (T Pa$^{-1}$) | $10^3 \cdot \alpha$ (K$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 2-Hydroxy Ethylammonium Formate (2-HEAF) | | | | | | | | | |
| 338.15 | 1.148091 | 1613.59 | 334.53 | 0.6188 | 321.15 | 1.160154 | 1653.63 | 315.22 | 0.6124 |
| 337.90 | 1.148254 | 1614.14 | 334.26 | 0.6187 | 320.91 | 1.160330 | 1654.22 | 314.94 | 0.6124 |
| 337.66 | 1.148433 | 1614.71 | 333.97 | 0.6186 | 320.66 | 1.160509 | 1654.81 | 314.67 | 0.6123 |
| 337.40 | 1.148608 | 1615.30 | 333.67 | 0.6185 | 320.40 | 1.160688 | 1655.41 | 314.39 | 0.6122 |
| 337.15 | 1.148785 | 1615.87 | 333.39 | 0.6184 | 320.15 | 1.160863 | 1656.01 | 314.12 | 0.6121 |
| 336.91 | 1.148963 | 1616.46 | 333.09 | 0.6183 | 319.90 | 1.161042 | 1656.60 | 313.85 | 0.6120 |
| 336.66 | 1.149139 | 1617.04 | 332.80 | 0.6182 | 319.65 | 1.161218 | 1657.19 | 313.58 | 0.6119 |
| 336.41 | 1.149316 | 1617.63 | 332.51 | 0.6182 | 319.40 | 1.161398 | 1657.79 | 313.30 | 0.6118 |
| 336.16 | 1.149494 | 1618.22 | 332.21 | 0.6181 | 319.15 | 1.161574 | 1658.39 | 313.03 | 0.6117 |
| 335.90 | 1.149669 | 1618.81 | 331.92 | 0.6180 | 318.91 | 1.161750 | 1658.98 | 312.76 | 0.6116 |
| 335.65 | 1.149848 | 1619.38 | 331.64 | 0.6179 | 318.65 | 1.161930 | 1659.58 | 312.48 | 0.6115 |
| 335.40 | 1.150027 | 1619.96 | 331.35 | 0.6178 | 318.40 | 1.162110 | 1660.18 | 312.21 | 0.6114 |
| 335.16 | 1.150205 | 1620.55 | 331.05 | 0.6177 | 318.16 | 1.162286 | 1660.78 | 311.93 | 0.6113 |
| 334.90 | 1.150384 | 1621.13 | 330.77 | 0.6176 | 317.90 | 1.162462 | 1661.37 | 311.67 | 0.6112 |
| 334.66 | 1.150560 | 1621.71 | 330.48 | 0.6175 | 317.65 | 1.162643 | 1661.97 | 311.39 | 0.6111 |
| 334.40 | 1.150740 | 1622.30 | 330.19 | 0.6174 | 317.41 | 1.162820 | 1662.56 | 311.12 | 0.6110 |
| 334.16 | 1.150916 | 1622.89 | 329.90 | 0.6173 | 317.15 | 1.162998 | 1663.16 | 310.85 | 0.6109 |
| 333.90 | 1.151094 | 1623.48 | 329.61 | 0.6173 | 316.91 | 1.163174 | 1663.75 | 310.58 | 0.6108 |
| 333.65 | 1.151271 | 1624.06 | 329.32 | 0.6172 | 316.65 | 1.163352 | 1664.35 | 310.31 | 0.6107 |
| 333.41 | 1.151449 | 1624.64 | 329.03 | 0.6171 | 316.41 | 1.163529 | 1664.95 | 310.04 | 0.6106 |
| 333.16 | 1.151625 | 1625.23 | 328.75 | 0.6170 | 316.15 | 1.163706 | 1665.55 | 309.77 | 0.6105 |
| 332.90 | 1.151804 | 1625.82 | 328.46 | 0.6169 | 315.90 | 1.163885 | 1666.15 | 309.50 | 0.6104 |
| 332.65 | 1.151981 | 1626.41 | 328.17 | 0.6168 | 315.65 | 1.164062 | 1666.74 | 309.23 | 0.6103 |
| 332.41 | 1.152159 | 1626.99 | 327.88 | 0.6167 | 315.40 | 1.164240 | 1667.34 | 308.96 | 0.6102 |
| 332.15 | 1.152338 | 1627.58 | 327.59 | 0.6166 | 315.15 | 1.164417 | 1667.94 | 308.70 | 0.6101 |
| 331.90 | 1.152514 | 1628.16 | 327.31 | 0.6165 | 314.90 | 1.164597 | 1668.54 | 308.43 | 0.6100 |
| 331.65 | 1.152694 | 1628.75 | 327.02 | 0.6164 | 314.65 | 1.164774 | 1669.14 | 308.16 | 0.6099 |
| 331.40 | 1.152871 | 1629.34 | 326.74 | 0.6163 | 314.40 | 1.164951 | 1669.73 | 307.89 | 0.6098 |
| 331.16 | 1.153048 | 1629.93 | 326.45 | 0.6162 | 314.15 | 1.165128 | 1670.33 | 307.63 | 0.6097 |
| 330.90 | 1.153225 | 1630.52 | 326.16 | 0.6162 | 313.90 | 1.165305 | 1670.94 | 307.35 | 0.6096 |
| 330.65 | 1.153405 | 1631.11 | 325.88 | 0.6161 | 313.65 | 1.165485 | 1671.54 | 307.09 | 0.6095 |
| 330.41 | 1.153582 | 1631.69 | 325.59 | 0.6160 | 313.40 | 1.165661 | 1672.13 | 306.82 | 0.6094 |
| 330.15 | 1.153761 | 1632.29 | 325.30 | 0.6159 | 313.15 | 1.165839 | 1672.72 | 306.56 | 0.6093 |
| 329.90 | 1.153939 | 1632.88 | 325.02 | 0.6158 | 312.90 | 1.166018 | 1673.34 | 306.29 | 0.6092 |
| 329.65 | 1.154114 | 1633.47 | 324.73 | 0.6157 | 312.65 | 1.166194 | 1673.94 | 306.02 | 0.6091 |
| 329.41 | 1.154294 | 1634.06 | 324.45 | 0.6156 | 312.40 | 1.166372 | 1674.54 | 305.75 | 0.6090 |
| 329.15 | 1.154469 | 1634.65 | 324.17 | 0.6155 | 312.15 | 1.166549 | 1675.14 | 305.49 | 0.6089 |
| 328.91 | 1.154648 | 1635.24 | 323.88 | 0.6154 | 311.90 | 1.166726 | 1675.74 | 305.22 | 0.6088 |
| 328.65 | 1.154826 | 1635.84 | 323.59 | 0.6153 | 311.65 | 1.166903 | 1676.34 | 304.96 | 0.6086 |
| 328.40 | 1.155003 | 1636.43 | 323.31 | 0.6152 | 311.40 | 1.167085 | 1676.95 | 304.69 | 0.6085 |
| 328.15 | 1.155181 | 1637.02 | 323.03 | 0.6151 | 311.15 | 1.167260 | 1677.55 | 304.43 | 0.6084 |
| 327.90 | 1.155360 | 1637.61 | 322.75 | 0.6150 | 310.90 | 1.167437 | 1678.14 | 304.17 | 0.6083 |
| 327.66 | 1.155535 | 1638.20 | 322.47 | 0.6149 | 310.65 | 1.167617 | 1678.74 | 303.90 | 0.6082 |
| 327.40 | 1.155713 | 1638.79 | 322.18 | 0.6148 | 310.40 | 1.167794 | 1679.35 | 303.63 | 0.6081 |
| 327.16 | 1.155890 | 1639.38 | 321.90 | 0.6148 | 310.15 | 1.167970 | 1679.94 | 303.38 | 0.6080 |
| 326.91 | 1.156069 | 1639.97 | 321.62 | 0.6147 | 309.90 | 1.168149 | 1680.55 | 303.11 | 0.6079 |
| 326.66 | 1.156247 | 1640.57 | 321.34 | 0.6146 | 309.65 | 1.168325 | 1681.15 | 302.85 | 0.6078 |
| 326.41 | 1.156426 | 1641.16 | 321.06 | 0.6145 | 309.40 | 1.168502 | 1681.75 | 302.59 | 0.6077 |
| 326.16 | 1.156603 | 1641.75 | 320.78 | 0.6144 | 309.15 | 1.168680 | 1682.35 | 302.32 | 0.6076 |
| 325.91 | 1.156780 | 1642.34 | 320.50 | 0.6143 | 308.90 | 1.168859 | 1682.96 | 302.06 | 0.6075 |
| 325.65 | 1.156957 | 1642.94 | 320.21 | 0.6142 | 308.65 | 1.169036 | 1683.55 | 301.80 | 0.6074 |
| 325.40 | 1.157136 | 1643.53 | 319.93 | 0.6141 | 308.40 | 1.169213 | 1684.16 | 301.54 | 0.6073 |
| 325.16 | 1.157314 | 1644.12 | 319.66 | 0.6140 | 308.15 | 1.169391 | 1684.76 | 301.28 | 0.6072 |
| 324.90 | 1.157490 | 1644.72 | 319.37 | 0.6139 | 307.90 | 1.169567 | 1685.36 | 301.02 | 0.6071 |
| 324.65 | 1.157669 | 1645.32 | 319.09 | 0.6138 | 307.65 | 1.169742 | 1685.96 | 300.76 | 0.6070 |
| 324.40 | 1.157846 | 1645.91 | 318.81 | 0.6137 | 307.40 | 1.169922 | 1686.56 | 300.50 | 0.6069 |
| 324.15 | 1.158023 | 1646.50 | 318.54 | 0.6136 | 307.15 | 1.170102 | 1687.17 | 300.23 | 0.6068 |
| 323.90 | 1.158201 | 1647.09 | 318.26 | 0.6135 | 306.90 | 1.170276 | 1687.77 | 299.98 | 0.6067 |
| 323.65 | 1.158378 | 1647.68 | 317.98 | 0.6134 | 306.65 | 1.170454 | 1688.37 | 299.72 | 0.6066 |
| 323.40 | 1.158556 | 1648.28 | 317.70 | 0.6133 | 306.40 | 1.170632 | 1688.98 | 299.45 | 0.6065 |
| 323.15 | 1.158734 | 1648.90 | 317.42 | 0.6132 | 306.15 | 1.170810 | 1689.58 | 299.20 | 0.6064 |
| 322.90 | 1.158910 | 1649.47 | 317.15 | 0.6131 | 305.90 | 1.170986 | 1690.18 | 298.94 | 0.6063 |
| 322.66 | 1.159088 | 1650.06 | 316.87 | 0.6130 | 305.65 | 1.171165 | 1690.79 | 298.68 | 0.6062 |
| 322.41 | 1.159265 | 1650.66 | 316.59 | 0.6129 | 305.40 | 1.171343 | 1691.39 | 298.42 | 0.6060 |
| 322.16 | 1.159442 | 1651.25 | 316.32 | 0.6128 | 305.15 | 1.171518 | 1691.99 | 298.16 | 0.6059 |
| 321.91 | 1.159620 | 1651.85 | 316.04 | 0.6127 | 304.90 | 1.171699 | 1692.60 | 297.90 | 0.6058 |
| 321.65 | 1.159797 | 1652.43 | 315.77 | 0.6126 | 304.65 | 1.171876 | 1693.20 | 297.65 | 0.6057 |
| 321.40 | 1.159976 | 1653.03 | 315.49 | 0.6125 | 304.40 | 1.172053 | 1693.80 | 297.39 | 0.6056 |

**TABLE 2 (Continued)**

| $T$ (K) | $\rho$ (g cm$^{-3}$) | $u$ (m s$^{-1}$) | $\kappa_S$ (T Pa$^{-1}$) | $10^3 \cdot \alpha$ (K$^{-1}$) | $T$ (K) | $\rho$ (g cm$^{-3}$) | $u$ (m s$^{-1}$) | $\kappa_S$ (T Pa$^{-1}$) | $10^3 \cdot \alpha$ (K$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 2-Hydroxy Ethylammonium Formate (2-HEAF) | | | | | | | | | |
| 304.15 | 1.172230 | 1694.41 | 297.13 | 0.6055 | 291.15 | 1.181453 | 1726.18 | 284.06 | 0.5998 |
| 303.90 | 1.172408 | 1695.01 | 296.88 | 0.6054 | 290.90 | 1.181631 | 1726.80 | 283.81 | 0.5997 |
| 303.65 | 1.172587 | 1695.62 | 296.62 | 0.6053 | 290.65 | 1.181809 | 1727.43 | 283.56 | 0.5996 |
| 303.40 | 1.172764 | 1696.23 | 296.36 | 0.6052 | 290.40 | 1.181990 | 1728.05 | 283.32 | 0.5995 |
| 303.15 | 1.172937 | 1696.81 | 296.11 | 0.6051 | 290.15 | 1.182162 | 1728.67 | 283.07 | 0.5994 |
| 302.90 | 1.173120 | 1697.43 | 295.85 | 0.6050 | 289.90 | 1.182339 | 1729.29 | 282.83 | 0.5993 |
| 302.65 | 1.173295 | 1698.04 | 295.59 | 0.6049 | 289.65 | 1.182515 | 1729.91 | 282.58 | 0.5991 |
| 302.40 | 1.173473 | 1698.64 | 295.34 | 0.6048 | 289.39 | 1.182700 | 1730.84 | 282.24 | 0.5990 |
| 302.15 | 1.173648 | 1699.25 | 295.09 | 0.6047 | 289.15 | 1.182877 | 1731.59 | 281.95 | 0.5989 |
| 301.90 | 1.173826 | 1699.86 | 294.83 | 0.6046 | 288.89 | 1.183052 | 1732.13 | 281.73 | 0.5988 |
| 301.65 | 1.174003 | 1700.47 | 294.57 | 0.6045 | 288.64 | 1.183228 | 1732.78 | 281.48 | 0.5987 |
| 301.40 | 1.174180 | 1701.07 | 294.32 | 0.6043 | 288.39 | 1.183407 | 1733.34 | 281.25 | 0.5986 |
| 301.15 | 1.174361 | 1701.68 | 294.06 | 0.6042 | 288.15 | 1.183574 | 1733.91 | 281.03 | 0.5985 |
| 300.90 | 1.174535 | 1702.29 | 293.81 | 0.6041 | 287.90 | 1.183753 | 1734.51 | 280.79 | 0.5983 |
| 300.65 | 1.174714 | 1702.90 | 293.56 | 0.6040 | 287.64 | 1.183941 | 1735.04 | 280.58 | 0.5982 |
| 300.40 | 1.174891 | 1703.50 | 293.30 | 0.6039 | 287.40 | 1.184107 | 1735.67 | 280.33 | 0.5981 |
| 300.15 | 1.175070 | 1704.12 | 293.05 | 0.6038 | 287.15 | 1.184289 | 1736.27 | 280.10 | 0.5980 |
| 299.90 | 1.175247 | 1704.73 | 292.79 | 0.6037 | 286.90 | 1.184462 | 1736.82 | 279.88 | 0.5979 |
| 299.65 | 1.175425 | 1705.33 | 292.54 | 0.6036 | 286.65 | 1.184637 | 1737.45 | 279.63 | 0.5978 |
| 299.40 | 1.175602 | 1705.95 | 292.29 | 0.6035 | 286.40 | 1.184815 | 1738.07 | 279.39 | 0.5977 |
| 299.15 | 1.175780 | 1706.55 | 292.04 | 0.6034 | 286.15 | 1.184986 | 1738.68 | 279.16 | 0.5975 |
| 298.90 | 1.175955 | 1707.16 | 291.78 | 0.6033 | 285.90 | 1.185168 | 1739.24 | 278.93 | 0.5974 |
| 298.65 | 1.176133 | 1707.77 | 291.53 | 0.6032 | 285.65 | 1.185344 | 1739.86 | 278.69 | 0.5973 |
| 298.40 | 1.176311 | 1708.39 | 291.28 | 0.6030 | 285.40 | 1.185519 | 1740.47 | 278.46 | 0.5972 |
| 298.15 | 1.176489 | 1709.00 | 291.02 | 0.6029 | 285.15 | 1.185700 | 1741.08 | 278.22 | 0.5971 |
| 297.90 | 1.176666 | 1709.61 | 290.77 | 0.6028 | 284.90 | 1.185886 | 1741.82 | 277.94 | 0.5970 |
| 297.65 | 1.176842 | 1710.22 | 290.52 | 0.6027 | 284.64 | 1.186059 | 1742.42 | 277.71 | 0.5968 |
| 297.40 | 1.177019 | 1710.84 | 290.27 | 0.6026 | 284.40 | 1.186228 | 1742.99 | 277.49 | 0.5967 |
| 297.15 | 1.177201 | 1711.45 | 290.02 | 0.6025 | 284.15 | 1.186403 | 1743.61 | 277.25 | 0.5966 |
| 296.90 | 1.177373 | 1712.06 | 289.77 | 0.6024 | 283.90 | 1.186582 | 1744.21 | 277.02 | 0.5965 |
| 296.65 | 1.177553 | 1712.67 | 289.52 | 0.6023 | 283.65 | 1.186756 | 1744.84 | 276.78 | 0.5964 |
| 296.40 | 1.177729 | 1713.28 | 289.27 | 0.6022 | 283.40 | 1.186933 | 1745.46 | 276.54 | 0.5963 |
| 296.15 | 1.177905 | 1713.90 | 289.01 | 0.6021 | 283.15 | 1.187110 | 1746.08 | 276.30 | 0.5961 |
| 295.90 | 1.178085 | 1714.52 | 288.76 | 0.6019 | 282.90 | 1.187288 | 1746.70 | 276.06 | 0.5960 |
| 295.65 | 1.178265 | 1715.13 | 288.51 | 0.6018 | 282.65 | 1.187467 | 1747.32 | 275.82 | 0.5959 |
| 295.40 | 1.178438 | 1715.75 | 288.26 | 0.6017 | 282.40 | 1.187641 | 1747.95 | 275.59 | 0.5958 |
| 295.15 | 1.178617 | 1716.36 | 288.01 | 0.6016 | 282.15 | 1.187817 | 1748.57 | 275.35 | 0.5957 |
| 294.90 | 1.178798 | 1716.97 | 287.76 | 0.6015 | 281.90 | 1.187991 | 1749.20 | 275.11 | 0.5956 |
| 294.65 | 1.178971 | 1717.58 | 287.52 | 0.6014 | 281.65 | 1.188172 | 1749.83 | 274.87 | 0.5954 |
| 294.40 | 1.179148 | 1718.20 | 287.27 | 0.6013 | 281.40 | 1.188344 | 1750.39 | 274.66 | 0.5953 |
| 294.15 | 1.179325 | 1718.81 | 287.02 | 0.6012 | 280.90 | 1.188699 | 1751.60 | 274.19 | 0.5951 |
| 293.90 | 1.179505 | 1719.42 | 286.77 | 0.6011 | 280.65 | 1.188874 | 1752.24 | 273.95 | 0.5950 |
| 293.65 | 1.179682 | 1720.04 | 286.52 | 0.6009 | 280.40 | 1.189050 | 1752.86 | 273.72 | 0.5948 |
| 293.40 | 1.179858 | 1720.66 | 286.27 | 0.6008 | 280.15 | 1.189231 | 1753.49 | 273.48 | 0.5947 |
| 293.15 | 1.180037 | 1721.27 | 286.03 | 0.6007 | 279.90 | 1.189407 | 1754.12 | 273.24 | 0.5946 |
| 292.90 | 1.180210 | 1721.88 | 285.78 | 0.6006 | 279.65 | 1.189580 | 1754.75 | 273.01 | 0.5945 |
| 292.65 | 1.180390 | 1722.50 | 285.53 | 0.6005 | 279.40 | 1.189760 | 1755.38 | 272.77 | 0.5944 |
| 292.40 | 1.180568 | 1723.11 | 285.29 | 0.6004 | 279.15 | 1.189935 | 1756.03 | 272.53 | 0.5943 |
| 292.15 | 1.180744 | 1723.72 | 285.04 | 0.6003 | 278.90 | 1.190108 | 1756.62 | 272.31 | 0.5941 |
| 291.90 | 1.180923 | 1724.34 | 284.80 | 0.6002 | 278.65 | 1.190288 | 1757.23 | 272.08 | 0.5940 |
| 291.65 | 1.181104 | 1724.95 | 284.55 | 0.6000 | 278.40 | 1.190464 | 1757.88 | 271.83 | 0.5939 |
| 291.40 | 1.181278 | 1725.57 | 284.30 | 0.5999 | 278.15 | 1.190632 | 1758.50 | 271.60 | 0.5938 |
| 2-Hydroxy Diethylammonium Formate (2-HDEAF) | | | | | | | | | |
| 338.148 | 1.167306 | 1697.99 | 297.13 | 0.6294 | 334.399 | 1.169947 | 1708.24 | 292.91 | 0.6139 |
| 337.898 | 1.167485 | 1698.67 | 296.85 | 0.6283 | 334.149 | 1.170124 | 1708.92 | 292.63 | 0.6129 |
| 337.649 | 1.167660 | 1699.35 | 296.56 | 0.6272 | 333.899 | 1.170294 | 1709.58 | 292.37 | 0.6119 |
| 337.400 | 1.167838 | 1700.05 | 296.27 | 0.6261 | 333.651 | 1.170470 | 1710.26 | 292.09 | 0.6110 |
| 337.149 | 1.168016 | 1700.75 | 295.99 | 0.6251 | 333.398 | 1.170646 | 1710.94 | 291.81 | 0.6100 |
| 336.899 | 1.168195 | 1701.43 | 295.70 | 0.6240 | 333.149 | 1.170816 | 1711.61 | 291.54 | 0.6091 |
| 336.650 | 1.168369 | 1702.12 | 295.42 | 0.6230 | 332.898 | 1.170991 | 1712.28 | 291.27 | 0.6081 |
| 336.398 | 1.168546 | 1702.81 | 295.14 | 0.6219 | 332.650 | 1.171163 | 1712.95 | 291.00 | 0.6072 |
| 336.147 | 1.168724 | 1703.51 | 294.85 | 0.6209 | 332.399 | 1.171336 | 1713.60 | 290.74 | 0.6063 |
| 335.898 | 1.168897 | 1704.18 | 294.57 | 0.6199 | 332.149 | 1.171510 | 1714.26 | 290.47 | 0.6053 |
| 335.649 | 1.169072 | 1704.86 | 294.29 | 0.6189 | 331.899 | 1.171683 | 1714.92 | 290.20 | 0.6044 |
| 335.399 | 1.169250 | 1705.54 | 294.01 | 0.6179 | 331.648 | 1.171853 | 1715.58 | 289.94 | 0.6035 |
| 335.149 | 1.169423 | 1706.22 | 293.74 | 0.6169 | 331.399 | 1.172025 | 1716.23 | 289.68 | 0.6026 |
| 334.899 | 1.169602 | 1706.90 | 293.46 | 0.6159 | 331.150 | 1.172199 | 1716.88 | 289.41 | 0.6017 |
| 334.650 | 1.169774 | 1707.57 | 293.18 | 0.6149 | 330.898 | 1.172371 | 1717.54 | 289.15 | 0.6008 |

**TABLE 2 (Continued)**

| $T$ (K) | $\rho$ (g cm$^{-3}$) | $u$ (m s$^{-1}$) | $\kappa_S$ (T Pa$^{-1}$) | $10^3 \cdot \alpha$ (K$^{-1}$) | $T$ (K) | $\rho$ (g cm$^{-3}$) | $u$ (m s$^{-1}$) | $\kappa_S$ (T Pa$^{-1}$) | $10^3 \cdot \alpha$ (K$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 2-Hydroxy Diethylammonium Formate (2-HDEAF) | | | | | | | | | |
| 330.648 | 1.172539 | 1718.21 | 288.88 | 0.6000 | 313.649 | 1.183936 | 1760.64 | 272.48 | 0.5564 |
| 330.400 | 1.172712 | 1718.85 | 288.62 | 0.5991 | 313.398 | 1.184098 | 1761.26 | 272.25 | 0.5560 |
| 330.149 | 1.172885 | 1719.50 | 288.36 | 0.5982 | 313.147 | 1.184263 | 1761.87 | 272.02 | 0.5556 |
| 329.899 | 1.173052 | 1720.15 | 288.10 | 0.5974 | 312.898 | 1.184428 | 1762.48 | 271.80 | 0.5552 |
| 329.648 | 1.173226 | 1720.80 | 287.84 | 0.5965 | 312.648 | 1.184593 | 1763.09 | 271.57 | 0.5548 |
| 329.399 | 1.173398 | 1721.46 | 287.58 | 0.5957 | 312.397 | 1.184759 | 1763.71 | 271.34 | 0.5544 |
| 329.149 | 1.173566 | 1722.08 | 287.33 | 0.5948 | 312.148 | 1.184922 | 1764.32 | 271.12 | 0.5541 |
| 328.899 | 1.173737 | 1722.72 | 287.08 | 0.5940 | 311.897 | 1.185086 | 1764.94 | 270.89 | 0.5537 |
| 328.649 | 1.173908 | 1723.35 | 286.83 | 0.5932 | 311.647 | 1.185251 | 1765.54 | 270.67 | 0.5533 |
| 328.399 | 1.174079 | 1723.99 | 286.57 | 0.5923 | 311.399 | 1.185413 | 1766.15 | 270.44 | 0.5530 |
| 328.149 | 1.174248 | 1724.62 | 286.32 | 0.5915 | 311.148 | 1.185575 | 1766.76 | 270.22 | 0.5527 |
| 327.897 | 1.174417 | 1725.26 | 286.07 | 0.5907 | 310.897 | 1.185743 | 1767.37 | 269.99 | 0.5523 |
| 327.647 | 1.174587 | 1725.89 | 285.82 | 0.5899 | 310.647 | 1.185907 | 1767.99 | 269.77 | 0.5520 |
| 327.399 | 1.174757 | 1726.52 | 285.57 | 0.5891 | 310.398 | 1.186071 | 1768.60 | 269.54 | 0.5517 |
| 327.148 | 1.174928 | 1727.15 | 285.32 | 0.5884 | 310.148 | 1.186236 | 1769.20 | 269.32 | 0.5514 |
| 326.898 | 1.175096 | 1727.78 | 285.07 | 0.5876 | 309.897 | 1.186398 | 1769.82 | 269.10 | 0.5511 |
| 326.649 | 1.175266 | 1728.41 | 284.82 | 0.5868 | 309.647 | 1.186561 | 1770.43 | 268.88 | 0.5508 |
| 326.398 | 1.175433 | 1729.05 | 284.57 | 0.5861 | 309.398 | 1.186725 | 1771.04 | 268.65 | 0.5505 |
| 326.148 | 1.175605 | 1729.68 | 284.32 | 0.5853 | 309.147 | 1.186891 | 1771.65 | 268.43 | 0.5502 |
| 325.898 | 1.175771 | 1730.32 | 284.07 | 0.5846 | 308.898 | 1.187053 | 1772.26 | 268.21 | 0.5499 |
| 325.649 | 1.175942 | 1730.95 | 283.82 | 0.5838 | 308.648 | 1.187216 | 1772.87 | 267.99 | 0.5496 |
| 325.398 | 1.176111 | 1731.58 | 283.57 | 0.5831 | 308.399 | 1.187384 | 1773.48 | 267.77 | 0.5494 |
| 325.148 | 1.176280 | 1732.21 | 283.33 | 0.5823 | 308.146 | 1.187545 | 1774.09 | 267.55 | 0.5491 |
| 324.898 | 1.176448 | 1732.85 | 283.08 | 0.5816 | 307.898 | 1.187709 | 1774.69 | 267.33 | 0.5489 |
| 324.648 | 1.176614 | 1733.47 | 282.84 | 0.5809 | 307.647 | 1.187875 | 1775.30 | 267.11 | 0.5486 |
| 324.398 | 1.176781 | 1734.11 | 282.59 | 0.5802 | 307.397 | 1.188037 | 1775.91 | 266.89 | 0.5484 |
| 324.147 | 1.176950 | 1734.74 | 282.34 | 0.5795 | 307.147 | 1.188200 | 1776.53 | 266.66 | 0.5482 |
| 323.898 | 1.177123 | 1735.37 | 282.09 | 0.5788 | 306.897 | 1.188361 | 1777.13 | 266.45 | 0.5479 |
| 323.649 | 1.177289 | 1736.00 | 281.85 | 0.5781 | 306.647 | 1.188527 | 1777.74 | 266.23 | 0.5477 |
| 323.398 | 1.177455 | 1736.63 | 281.61 | 0.5775 | 306.397 | 1.188692 | 1778.34 | 266.01 | 0.5475 |
| 323.148 | 1.177621 | 1737.25 | 281.36 | 0.5768 | 306.148 | 1.188850 | 1778.95 | 265.79 | 0.5473 |
| 322.899 | 1.177790 | 1737.87 | 281.12 | 0.5761 | 305.897 | 1.189012 | 1779.55 | 265.58 | 0.5471 |
| 322.649 | 1.177958 | 1738.50 | 280.88 | 0.5755 | 305.647 | 1.189178 | 1780.17 | 265.36 | 0.5469 |
| 322.398 | 1.178124 | 1739.12 | 280.64 | 0.5748 | 305.397 | 1.189346 | 1780.80 | 265.13 | 0.5468 |
| 322.147 | 1.178293 | 1739.73 | 280.40 | 0.5742 | 305.148 | 1.189506 | 1781.40 | 264.92 | 0.5466 |
| 321.897 | 1.178462 | 1740.36 | 280.16 | 0.5735 | 304.897 | 1.189665 | 1782.01 | 264.70 | 0.5464 |
| 321.648 | 1.178624 | 1740.97 | 279.93 | 0.5729 | 304.648 | 1.189827 | 1782.61 | 264.49 | 0.5463 |
| 321.399 | 1.178792 | 1741.59 | 279.69 | 0.5723 | 304.397 | 1.189991 | 1783.22 | 264.27 | 0.5461 |
| 321.148 | 1.178961 | 1742.21 | 279.45 | 0.5717 | 304.147 | 1.190159 | 1783.83 | 264.05 | 0.5460 |
| 320.898 | 1.179128 | 1742.83 | 279.21 | 0.5710 | 303.898 | 1.190318 | 1784.45 | 263.83 | 0.5458 |
| 320.649 | 1.179294 | 1743.44 | 278.97 | 0.5704 | 303.648 | 1.190481 | 1785.05 | 263.62 | 0.5457 |
| 320.397 | 1.179459 | 1744.06 | 278.74 | 0.5698 | 303.397 | 1.190645 | 1785.67 | 263.40 | 0.5456 |
| 320.149 | 1.179628 | 1744.67 | 278.50 | 0.5693 | 303.148 | 1.190807 | 1786.27 | 263.19 | 0.5454 |
| 319.898 | 1.179795 | 1745.29 | 278.26 | 0.5687 | 302.897 | 1.190966 | 1786.88 | 262.97 | 0.5453 |
| 319.648 | 1.179965 | 1745.90 | 278.03 | 0.5681 | 302.647 | 1.191134 | 1787.50 | 262.75 | 0.5452 |
| 319.398 | 1.180128 | 1746.51 | 277.80 | 0.5675 | 302.397 | 1.191295 | 1788.11 | 262.54 | 0.5451 |
| 319.148 | 1.180293 | 1747.14 | 277.56 | 0.5670 | 302.146 | 1.191456 | 1788.72 | 262.32 | 0.5450 |
| 318.897 | 1.180461 | 1747.75 | 277.33 | 0.5664 | 301.898 | 1.191616 | 1789.33 | 262.11 | 0.5450 |
| 318.648 | 1.180625 | 1748.37 | 277.09 | 0.5659 | 301.645 | 1.191779 | 1789.94 | 261.90 | 0.5449 |
| 318.398 | 1.180791 | 1748.99 | 276.85 | 0.5653 | 301.397 | 1.191946 | 1790.55 | 261.68 | 0.5448 |
| 318.148 | 1.180960 | 1749.60 | 276.62 | 0.5648 | 301.148 | 1.192106 | 1791.16 | 261.47 | 0.5447 |
| 317.898 | 1.181123 | 1750.21 | 276.39 | 0.5643 | 300.898 | 1.192269 | 1791.77 | 261.25 | 0.5447 |
| 317.648 | 1.181290 | 1750.83 | 276.16 | 0.5637 | 300.648 | 1.192428 | 1792.39 | 261.04 | 0.5446 |
| 317.397 | 1.181457 | 1751.44 | 275.93 | 0.5632 | 300.397 | 1.192595 | 1793.00 | 260.82 | 0.5446 |
| 317.147 | 1.181622 | 1752.06 | 275.69 | 0.5627 | 300.148 | 1.192754 | 1793.62 | 260.61 | 0.5446 |
| 316.898 | 1.181787 | 1752.68 | 275.46 | 0.5622 | 299.897 | 1.192914 | 1794.23 | 260.40 | 0.5445 |
| 316.646 | 1.181953 | 1753.29 | 275.23 | 0.5617 | 299.648 | 1.193072 | 1794.84 | 260.18 | 0.5445 |
| 316.398 | 1.182120 | 1753.91 | 274.99 | 0.5612 | 299.397 | 1.193240 | 1795.46 | 259.97 | 0.5445 |
| 316.148 | 1.182282 | 1754.52 | 274.77 | 0.5608 | 299.148 | 1.193403 | 1796.07 | 259.76 | 0.5445 |
| 315.897 | 1.182447 | 1755.13 | 274.54 | 0.5603 | 298.897 | 1.193563 | 1796.69 | 259.54 | 0.5445 |
| 315.648 | 1.182618 | 1755.75 | 274.30 | 0.5598 | 298.647 | 1.193724 | 1797.31 | 259.33 | 0.5445 |
| 315.397 | 1.182779 | 1756.36 | 274.07 | 0.5594 | 298.398 | 1.193889 | 1797.92 | 259.12 | 0.5445 |
| 315.148 | 1.182944 | 1756.97 | 273.85 | 0.5589 | 298.148 | 1.194041 | 1798.54 | 258.91 | 0.5445 |
| 314.898 | 1.183111 | 1757.58 | 273.62 | 0.5585 | 297.897 | 1.194211 | 1799.17 | 258.69 | 0.5446 |
| 314.648 | 1.183277 | 1758.20 | 273.39 | 0.5580 | 297.647 | 1.194365 | 1799.77 | 258.48 | 0.5446 |
| 314.398 | 1.183441 | 1758.81 | 273.16 | 0.5576 | 297.398 | 1.194529 | 1800.39 | 258.27 | 0.5446 |
| 314.148 | 1.183605 | 1759.42 | 272.93 | 0.5572 | 297.145 | 1.194689 | 1801.02 | 258.05 | 0.5447 |
| 313.897 | 1.183770 | 1760.03 | 272.70 | 0.5568 | 296.897 | 1.194853 | 1801.63 | 257.84 | 0.5447 |

**TABLE 2 (Continued)**

| $T$ (K) | $\rho$ (g cm$^{-3}$) | $u$ (m s$^{-1}$) | $\kappa_S$ (T Pa$^{-1}$) | $10^3 \cdot \alpha$ (K$^{-1}$) | $T$ (K) | $\rho$ (g cm$^{-3}$) | $u$ (m s$^{-1}$) | $\kappa_S$ (T Pa$^{-1}$) | $10^3 \cdot \alpha$ (K$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 2-Hydroxy Diethylammonium Formate (2-HDEAF) | | | | | | | | | |
| 296.647 | 1.195012 | 1802.25 | 257.63 | 0.5448 | 287.145 | 1.201254 | 1826.68 | 249.48 | 0.5523 |
| 296.397 | 1.195176 | 1802.87 | 257.42 | 0.5449 | 286.895 | 1.201421 | 1827.35 | 249.27 | 0.5526 |
| 296.146 | 1.195335 | 1803.50 | 257.20 | 0.5449 | 286.647 | 1.201589 | 1827.98 | 249.06 | 0.5529 |
| 295.897 | 1.195495 | 1804.12 | 256.99 | 0.5450 | 286.395 | 1.201757 | 1828.65 | 248.84 | 0.5533 |
| 295.647 | 1.195653 | 1804.76 | 256.78 | 0.5451 | 286.146 | 1.201924 | 1829.30 | 248.63 | 0.5536 |
| 295.396 | 1.195819 | 1805.38 | 256.56 | 0.5452 | 285.897 | 1.202093 | 1829.97 | 248.41 | 0.5540 |
| 295.146 | 1.195977 | 1806.02 | 256.35 | 0.5453 | 285.647 | 1.202258 | 1830.61 | 248.21 | 0.5544 |
| 294.897 | 1.196138 | 1806.66 | 256.13 | 0.5454 | 285.396 | 1.202428 | 1831.29 | 247.99 | 0.5547 |
| 294.647 | 1.196296 | 1807.32 | 255.91 | 0.5455 | 285.146 | 1.202594 | 1831.96 | 247.77 | 0.5551 |
| 294.397 | 1.196455 | 1807.97 | 255.69 | 0.5457 | 284.897 | 1.202763 | 1832.62 | 247.56 | 0.5555 |
| 294.147 | 1.196617 | 1808.61 | 255.48 | 0.5458 | 284.646 | 1.202928 | 1833.29 | 247.34 | 0.5559 |
| 293.896 | 1.196776 | 1809.26 | 255.26 | 0.5459 | 284.395 | 1.203095 | 1833.93 | 247.14 | 0.5563 |
| 293.647 | 1.196937 | 1809.92 | 255.04 | 0.5461 | 284.144 | 1.203261 | 1834.65 | 246.91 | 0.5567 |
| 293.397 | 1.197094 | 1810.56 | 254.83 | 0.5462 | 283.894 | 1.203428 | 1835.36 | 246.68 | 0.5571 |
| 293.147 | 1.197254 | 1811.20 | 254.61 | 0.5464 | 283.645 | 1.203596 | 1836.04 | 246.46 | 0.5576 |
| 292.896 | 1.197415 | 1811.83 | 254.40 | 0.5466 | 283.395 | 1.203761 | 1836.72 | 246.25 | 0.5580 |
| 292.647 | 1.197569 | 1812.48 | 254.19 | 0.5467 | 283.143 | 1.203931 | 1837.43 | 246.02 | 0.5584 |
| 292.396 | 1.197728 | 1813.12 | 253.97 | 0.5469 | 282.895 | 1.204097 | 1838.10 | 245.81 | 0.5589 |
| 292.146 | 1.197893 | 1813.76 | 253.76 | 0.5471 | 282.646 | 1.204263 | 1838.77 | 245.60 | 0.5593 |
| 291.896 | 1.198060 | 1814.40 | 253.55 | 0.5473 | 282.395 | 1.204429 | 1839.48 | 245.37 | 0.5598 |
| 291.647 | 1.198230 | 1815.03 | 253.33 | 0.5475 | 282.145 | 1.204596 | 1840.18 | 245.15 | 0.5602 |
| 291.397 | 1.198397 | 1815.67 | 253.12 | 0.5477 | 281.896 | 1.204763 | 1840.87 | 244.94 | 0.5607 |
| 291.147 | 1.198567 | 1816.31 | 252.91 | 0.5479 | 281.645 | 1.204932 | 1841.56 | 244.72 | 0.5612 |
| 290.897 | 1.198735 | 1816.95 | 252.69 | 0.5481 | 281.395 | 1.205098 | 1842.24 | 244.50 | 0.5617 |
| 290.647 | 1.198902 | 1817.59 | 252.48 | 0.5484 | 281.145 | 1.205262 | 1842.96 | 244.28 | 0.5622 |
| 290.395 | 1.199069 | 1818.23 | 252.27 | 0.5486 | 280.896 | 1.205430 | 1843.66 | 244.06 | 0.5627 |
| 290.146 | 1.199239 | 1818.89 | 252.05 | 0.5488 | 280.645 | 1.205596 | 1844.35 | 243.84 | 0.5632 |
| 289.896 | 1.199407 | 1819.53 | 251.83 | 0.5491 | 280.397 | 1.205766 | 1845.06 | 243.62 | 0.5637 |
| 289.647 | 1.199575 | 1820.18 | 251.62 | 0.5493 | 280.146 | 1.205932 | 1845.77 | 243.40 | 0.5642 |
| 289.396 | 1.199742 | 1820.81 | 251.41 | 0.5496 | 279.896 | 1.206098 | 1846.49 | 243.18 | 0.5647 |
| 289.146 | 1.199912 | 1821.48 | 251.19 | 0.5499 | 279.647 | 1.206263 | 1847.20 | 242.96 | 0.5652 |
| 288.896 | 1.200079 | 1822.12 | 250.98 | 0.5501 | 279.398 | 1.206429 | 1847.90 | 242.74 | 0.5658 |
| 288.645 | 1.200248 | 1822.76 | 250.77 | 0.5504 | 279.143 | 1.206595 | 1848.72 | 242.49 | 0.5663 |
| 288.396 | 1.200415 | 1823.41 | 250.55 | 0.5507 | 278.894 | 1.206764 | 1849.50 | 242.25 | 0.5669 |
| 288.146 | 1.200583 | 1824.08 | 250.33 | 0.5510 | 278.645 | 1.206928 | 1850.24 | 242.03 | 0.5674 |
| 287.895 | 1.200751 | 1824.72 | 250.12 | 0.5513 | 278.398 | 1.207096 | 1850.97 | 241.80 | 0.5680 |
| 287.647 | 1.200919 | 1825.36 | 249.91 | 0.5516 | 278.153 | 1.207250 | 1851.77 | 241.56 | 0.5686 |
| 287.396 | 1.201085 | 1826.02 | 249.70 | 0.5520 | | | | | |
| 2-Hydroxy Triethylammonium Formate (2-HTEAF) | | | | | | | | | |
| 338.145 | 1.212896 | 1841.05 | 243.25 | 0.5350944 | 330.646 | 1.217655 | 1863.53 | 236.48 | 0.50054876 |
| 337.895 | 1.213056 | 1841.81 | 243.01 | 0.53473476 | 330.396 | 1.217805 | 1864.27 | 236.27 | 0.49855042 |
| 337.645 | 1.213219 | 1842.58 | 242.78 | 0.53432049 | 330.145 | 1.217959 | 1864.99 | 236.06 | 0.49648913 |
| 337.395 | 1.213378 | 1843.35 | 242.54 | 0.53385159 | 329.895 | 1.218108 | 1865.71 | 235.84 | 0.4943813 |
| 337.146 | 1.213544 | 1844.12 | 242.31 | 0.53333026 | 329.645 | 1.218259 | 1866.43 | 235.63 | 0.49221885 |
| 336.896 | 1.213708 | 1844.88 | 242.07 | 0.53275232 | 329.397 | 1.218404 | 1867.15 | 235.42 | 0.49001972 |
| 336.645 | 1.213868 | 1845.63 | 241.85 | 0.53211711 | 329.145 | 1.218554 | 1867.87 | 235.21 | 0.48773006 |
| 336.396 | 1.214032 | 1846.42 | 241.61 | 0.53143254 | 328.896 | 1.218703 | 1868.59 | 235.00 | 0.48541312 |
| 336.146 | 1.214193 | 1847.15 | 241.38 | 0.53069071 | 328.646 | 1.218852 | 1869.31 | 234.79 | 0.48303237 |
| 335.895 | 1.214351 | 1847.91 | 241.15 | 0.52989095 | 328.397 | 1.219001 | 1870.02 | 234.59 | 0.48060683 |
| 335.646 | 1.214509 | 1848.66 | 240.93 | 0.52904314 | 328.146 | 1.219150 | 1870.74 | 234.38 | 0.47810696 |
| 335.394 | 1.214673 | 1849.43 | 240.69 | 0.52812995 | 327.896 | 1.219292 | 1871.45 | 234.17 | 0.47556231 |
| 335.146 | 1.214836 | 1850.18 | 240.47 | 0.52717706 | 327.644 | 1.219438 | 1872.13 | 233.97 | 0.47294202 |
| 334.895 | 1.214998 | 1850.94 | 240.24 | 0.5261579 | 327.394 | 1.219578 | 1872.86 | 233.77 | 0.47028767 |
| 334.646 | 1.215155 | 1851.69 | 240.01 | 0.52509245 | 327.144 | 1.219719 | 1873.58 | 233.56 | 0.4675787 |
| 334.396 | 1.215312 | 1852.43 | 239.79 | 0.5239682 | 326.894 | 1.219862 | 1874.29 | 233.35 | 0.46481509 |
| 334.146 | 1.215469 | 1853.19 | 239.56 | 0.52278932 | 326.645 | 1.220003 | 1874.99 | 233.15 | 0.46200823 |
| 333.896 | 1.215629 | 1853.93 | 239.34 | 0.52155581 | 326.144 | 1.220277 | 1876.42 | 232.75 | 0.45619648 |
| 333.646 | 1.215784 | 1854.69 | 239.11 | 0.52026767 | 325.896 | 1.220417 | 1877.12 | 232.55 | 0.45323842 |
| 333.395 | 1.215943 | 1855.43 | 238.89 | 0.51891941 | 325.646 | 1.220557 | 1877.82 | 232.35 | 0.45020209 |
| 333.146 | 1.216101 | 1856.17 | 238.67 | 0.51752749 | 325.395 | 1.220700 | 1878.52 | 232.15 | 0.44709866 |
| 332.895 | 1.216262 | 1856.90 | 238.45 | 0.51606954 | 325.145 | 1.220843 | 1879.22 | 231.94 | 0.44395286 |
| 332.644 | 1.216419 | 1857.67 | 238.22 | 0.51455651 | 324.896 | 1.220977 | 1879.93 | 231.74 | 0.44076533 |
| 332.395 | 1.216577 | 1858.41 | 238.00 | 0.51300114 | 324.647 | 1.221112 | 1880.63 | 231.55 | 0.43752361 |
| 332.145 | 1.216728 | 1859.14 | 237.78 | 0.51138499 | 324.396 | 1.221251 | 1881.31 | 231.35 | 0.43420101 |
| 331.895 | 1.216882 | 1859.88 | 237.56 | 0.50971422 | 324.148 | 1.221380 | 1881.98 | 231.16 | 0.43086403 |
| 331.645 | 1.217039 | 1860.62 | 237.35 | 0.50798881 | 323.894 | 1.221502 | 1882.65 | 230.98 | 0.42739059 |
| 331.396 | 1.217189 | 1861.35 | 237.13 | 0.506216 | 323.646 | 1.221627 | 1883.34 | 230.78 | 0.42394479 |
| 331.146 | 1.217344 | 1862.07 | 236.92 | 0.50438155 | 323.397 | 1.221756 | 1884.00 | 230.60 | 0.42043101 |
| 330.896 | 1.217498 | 1862.80 | 236.70 | 0.50249247 | 323.151 | 1.221864 | 1884.60 | 230.43 | 0.41690634 |

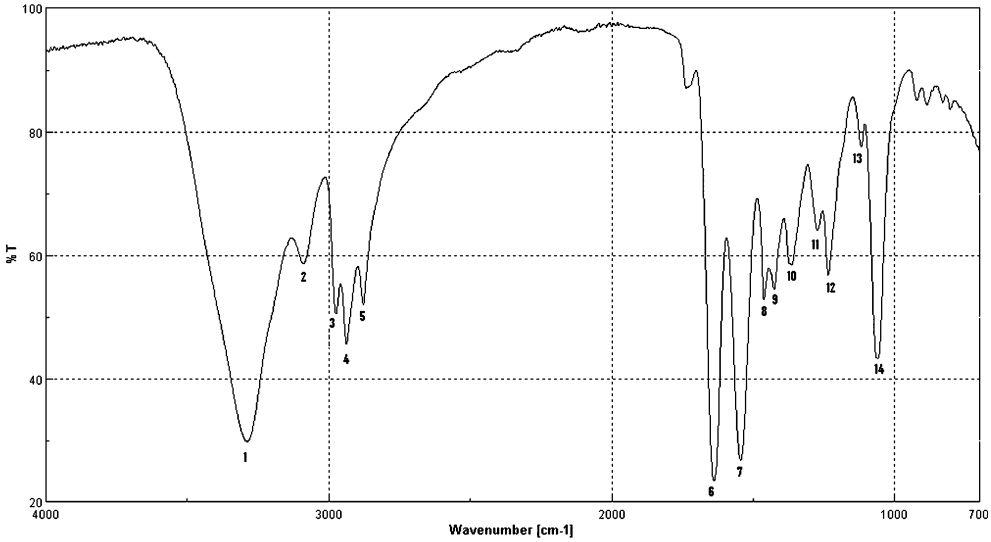



**Figure 1.** FT-IR spectra for 2HDEAF.

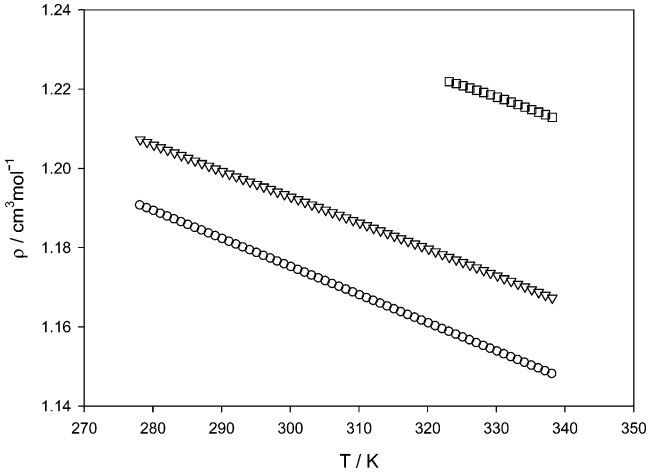



**Figure 2.** Curves of density (g cm$^{-3}$) of the studied ionic liquids (○) 2-HEAF, (▽) 2-HDEAF, and (□) 2-HTEAF in the range of temperature 278.15−338.15 K.

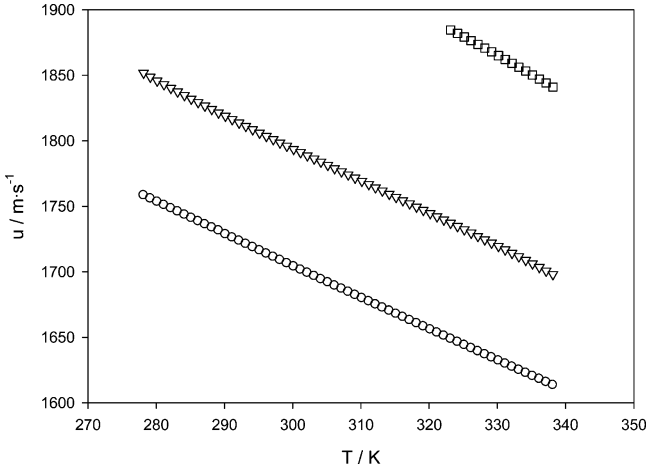



**Figure 3.** Curves of ultrasonic velocity (m s$^{-1}$) of the studied ionic liquids (○) 2-HEAF, (▽) 2-HDEAF, and (□) 2-HTEAF in the range of temperature 278.15−338.15 K.

neutralization product of 2-HEAA, which shows two characteristic bands at 3500−2400 cm$^{-1}$ for $NH_3^+ + OH^-$ and another wide band at 1600 cm$^{-1}$ for $COO^- + N-H$ plane bend.

**Catalytic Test.** The reactions were performed in liquid phase using a 100 mL batch reactor equipped with a condenser system, under argon atmosphere, in order to avoid $CO_2$. To a stirred solution of substrate and ketone (ratio ketone/substrate = 4.4) was added 1 g of ionic liquid, and the flask was maintained at 333.15 K using a water 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 × 0.32 mm × 0.25 $\mu$m). Tetradecane was used as the internal standard. Reagents were purchase from Aldrich and used without further purification

### Thermodynamic Data Treatment

For compact and smooth representation, the measured magnitudes of the ionic liquids were correlated as a function of temperature in accordance to eq 1:

$$P = \sum_{i=0}^{N} A_i T^i \qquad (1)$$

where $P$ is density (g cm$^{-3}$), ultrasonic velocity (m s$^{-1}$), or ionic conductivity ($\mu$S cm$^{-1}$), $A_i$ represents fitting parameters, and T is the absolute temperature. $N$ stands for the extension of the mathematical series. The fitting parameters were obtained by the unweighted least-squared method applying a fitting Marquardt algorithm. The root-mean-square deviations were computed using eq 2, where $z$ is the value of the property, and $n_{DAT}$ is the number of experimental data:

$$\sigma = \left( \frac{\sum_{i=1}^{n_{DAT}} (z_{exp} - z_{pred})^2}{n_{DAT}} \right)^{1/2} \qquad (2)$$

Densities and ultrasonic velocities are given in Table 2, and ionic conductivity is given in Table 3. The fitting parameters and the corresponding deviations are gathered in Table 4, which were computed as explained above. In Figures 2−4, the temperature trends of these magnitudes are gathered. These figures show a decreasing trend in the packing efficiency of the ionic liquids as the molecular weight rises. This tendency results in a continuous diminution of density and ultrasonic velocity versus temperature in each case. In Figure 4, the ionic conductivity of the ionic liquids is enclosed, where a rising trend

**TABLE 3: Values of Ionic Conductivity ($\mu$S/cm) of the Ionic Liquids in the Range 278.15−338.15 K**

| | 2-HEAF | 2-HDEAF | | 2-HTEAF |
|---|---|---|---|---|
| 278.15 K | 2158.20 | 452.76 | 323.15 K | 1843.38 |
| 288.15 K | 3069.00 | 676.17 | 325.65 K | 1975.05 |
| 298.15 K | 4197.60 | 973.17 | 328.15 K | 2108.7 |
| 308.15 K | 5623.20 | 1314.72 | 330.65 K | 2316.6 |
| 318.15 K | 6959.70 | 1707.75 | 333.15 K | 2494.8 |
| 328.15 K | 8563.50 | 2108.70 | 335.65 K | 2643.3 |
| 338.15 K | 10404.90 | 2395.80 | 338.15 K | 2811.6 |

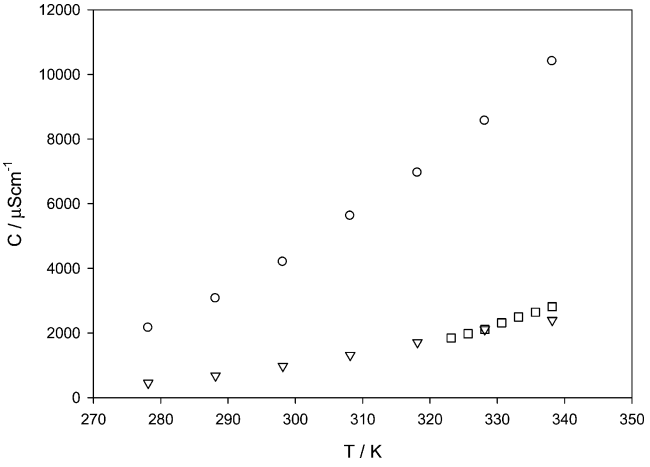



**Figure 4.** Curves of ionic conductivity ($\mu$S cm$^{-1}$) of the studied ionic liquids (○) 2-HEAF, (▽) 2-HDEAF, and (□) 2-HTEAF in the range of temperature 278.15−338.15 K.

for higher temperatures could be observed. This fact may be ascribed to the increasing mobility of ions for rising temperatures.

A frequently applied derived magnitude for industrial mixtures is the temperature dependence of volumetry, which is expressed as isobaric expansibility or a thermal expansion coefficient ($\alpha$). The data reported in literature normally give only values of thermal expansion coefficients both of pure compounds and their mixtures, showing the relative changes in density, 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

$$\alpha = -\left(\frac{\partial \ln \rho}{\partial T}\right)_{P,x} \tag{3}$$

taking into account the temperature dependence of density. These values are included in Table 2 and show a rising trend for each case (Figure 5). 2-HDEAF shows a minimum at 298.90 K. The other ionic liquids show a rising tendency with temperature.

## Catalytic Studies

In order to determine the catalytic activity of these ionic liquids, three model reactions were employed: citral−acetone condensation, condensation between benzaldehyde and acetone, and benzaldehyde and heptanal condensation. The ionic liquids studied were those included in this work (2-HEAF and 2-HDEAF; no experiments were realized with 2-HTEAF), as commented above, and others of the same family (2-HEAA, 2-HDEAA, 2-HTEAA, 2-HEAP, 2-HDEAP, and 2-HTEAP). Experimental data related to these compounds could be obtained from an earlier work.

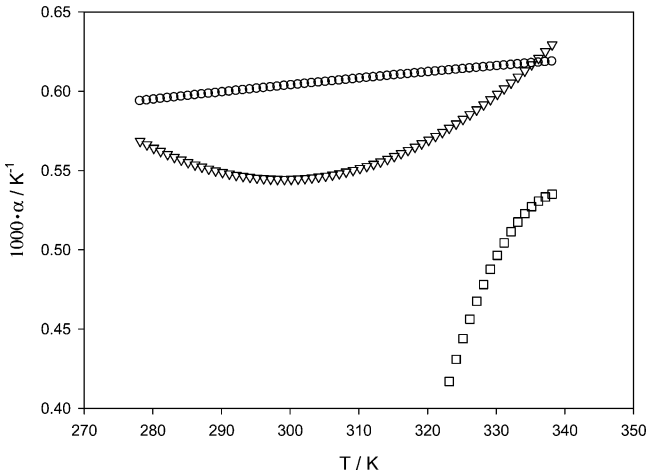



**Figure 5.** Curves of isobaric expansibility ($K^{-1}$) of the studied ionic liquids (○) 2-HEAF, (▽) 2-HDEAF, and (□) 2-HTEAF in the range of temperature 278.15−338.15 K.

The condensation reaction between citral and acetone (Scheme 1) leads to the formation of pseudoionone, which is an intermediate in the commercial production of vitamin A.

Citral consists of two isomers, neral and geranial, caused by the cis−trans isomerism at the C=C bond near the aldehyde group.[8]

The two isomers of citral can be converted into the corresponding pseudoionone with good selectivity (between 63 and 82%; Figure 6); the most active ionic liquid for this reaction is 2-HEAA, which gives a conversion of 52.3%, and the less active liquid is 2-HEAF, which gives a conversion of 34.8%. 2-HEAP gives an intermediate conversion of 40.2%.

Other compounds observed were those from the condensation of two citral molecules or of pseudoionone isomers and one acetone molecule.[11]

The catalytic activity of the ionic liquids was also tested in the production of benzylidenacetone (Scheme 2) from the condensation between benzaldehyde and acetone.

After 3 h, a conversion of 100% and a selectivity of 86% were obtained using 2-HEAP as the catalyst. Good conversions were also obtained with 2-HEAF (94.1%) and 2-HEAA (99.4%), with selectivities of 82% and 85%, respectively, after 4 h of reaction time (Figure 7). In these reactions, good conversions were obtained with all the ionic liquids in a relatively short time.

The third reaction for which the catalytic activity was studied was the synthesis of jasminaldhyde from the condensation between benzaldehyde and heptanal (Scheme 3).

In this reaction, good conversion was obtained with 2-HEAF (77.8%) and 2-HEAA (63.3%), while, with 2-HEAP, a lower conversion (18.5%) was obtained (Figure 8).

The selectivity was low (between 13.7% and 30.7%) because of the formation of a secondary product. The undesired product comes from the self-condensation of heptanal to 2-*n*-pentyl-2-nonenal, and this secondary reaction can be inhibited to some extent by the slow addition of heptanal.

We can conclude that, with this new synthesized ionic liquids family, good results were obtained in terms of conversion and selectivity for aldol condensation reactions. The ionic liquids are not soluble in the reaction mixture, so, at the end of the reaction, these catalysts are easy to separate from the reaction mixture. For future work, we intend to study the optimized recovery process of the catalysts and their reuse in repeated

**TABLE 4: Fitting Parameters for Density, Ultrasonic Velocity, and Conductivity of Eq 1 in the Range 278.15−338.15 K and Root-Mean-Square Deviations ($\sigma$) in Accordance with Eq 2 for Pure Ionic Liquids**

| | 2-HEAF | |
|---|---|---|
| | $\rho$/(g cm$^{-3}$) | $\sigma$ |
| $A_0$ | 1.3553 | $2.551 \times 10^{-6}$ |
| $A_1$ | −4.0096e-4 | |
| $A_2$ | −9.6623e-7 | |
| $A_3$ | 1.0048e-9 | |
| | $u$/(m s$^{-1}$) | $\sigma$ |
| $A_0$ | 2654.5515 | 0.065 |
| $A_1$ | −4.1691 | |
| $A_2$ | 4.2548e-3 | |
| $A_3$ | −3.0446e-6 | |
| | $C$/($\mu$S cm$^{-1}$) | $\sigma$ |
| $A_0$ | 48576.9035 | 45.817 |
| $A_1$ | −443.1112 | |
| $A_2$ | 1.0691 | |
| $A_3$ | −2.7428e-4 | |
| | 2-HDEAF | |
| | $\rho$/(g cm$^{-3}$) | $\sigma$ |
| $A_0$ | 1.8296 | $1.795 \times 10^{-5}$ |
| $A_1$ | −5.0300e-3 | |
| $A_2$ | 1.4476e-5 | |
| $A_3$ | −1.5950e-8 | |
| | $u$/(m s$^{-1}$) | $\sigma$ |
| $A_0$ | 6693.4496 | 0.058 |
| $A_1$ | −42.7907 | |
| $A_2$ | 0.1302 | |
| $A_3$ | −1.3999e-4 | |
| | $C$/($\mu$S cm$^{-1}$) | $\sigma$ |
| $A_0$ | 182372.1191 | 12.493 |
| $A_1$ | −1804.0674 | |
| $A_2$ | 5.8659 | |
| $A_3$ | −6.2241e-3 | |
| | 2-HTEAF[a] | |
| | $\rho$/(g cm$^{-3}$) | $\sigma$ |
| $A_0$ | −5.5873 | $4.959 \times 10^{-3}$ |
| $A_1$ | 0.0614 | |
| $A_2$ | −1.8296e-4 | |
| $A_3$ | 1.7976e-7 | |
| | $u$/(m s$^{-1}$) | $\sigma$ |
| $A_0$ | −2426.8628 | 0.018 |
| $A_1$ | 40.8934 | |
| $A_2$ | −0.1208 | |
| $A_3$ | 1.1000e-4 | |
| | $C$/($\mu$S cm$^{-1}$) | $\sigma$ |
| $A_0$ | 5610627.3132 | 11.158 |
| $A_1$ | −50905.4365 | |
| $A_2$ | 153.7971 | |
| $A_3$ | −0.1547 | |

[a] Within a temperature range of 338.15−323.15 K.

runs of experiments, which makes accurate experimental data on liquid−liquid-phase equilibrium among all related chemicals necessary.

## Results and Discussion

The basic physicochemical data of ionic liquids are important for the design of cleaner technological processes and a better

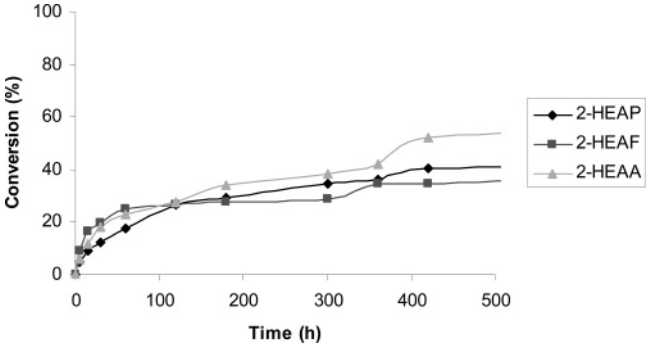



**Figure 6.** Conversion of citral in the citral−acetone condensation.

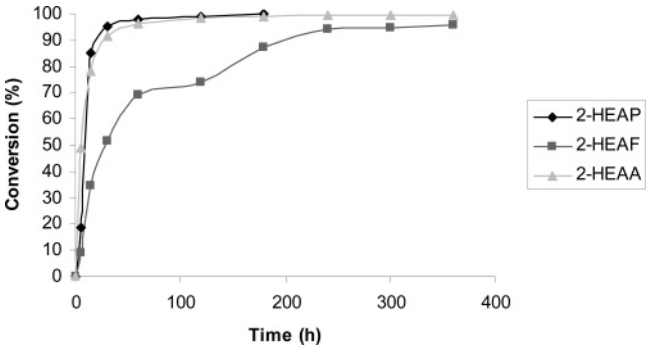
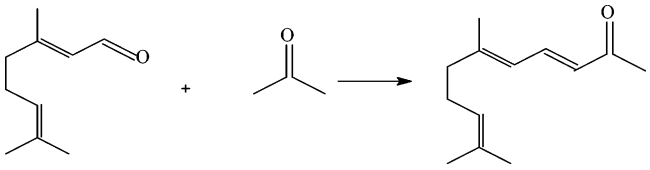
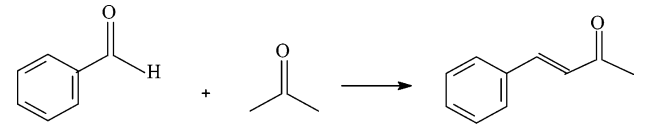



**Figure 7.** Conversion of benzaldehyde in the benzaldehyde−acetone condensation.

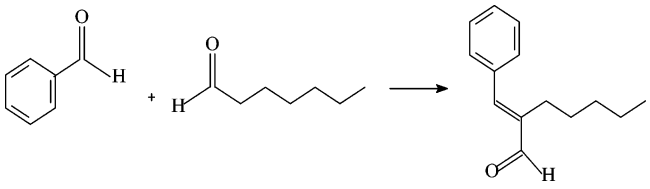
**SCHEME 1: Condensation Reaction between Citral and Acetone**



**SCHEME 2: Condensation Reaction between Benzaldehyde and Acetone**



**SCHEME 3: Condensation Reaction between Benzaldehyde and Heptanal**



understanding of the interactions in this kind of compound. In the present paper, we have presented a new synthesis and experimental data of the densities, ultrasonic velocities, and ionic conductivities of 2-HEAF, 2-HDEAF, and 2-HTEAF, which show liquid ionic characteristics according to the FT-IR results. No information on all these compounds is gathered in the literature as far as we know. From these results, the following was found:

1. An increase in temperature diminishes the interaction among ions, with lower values of density and ultrasonic velocity being gathered for rising temperatures in each case. At the same

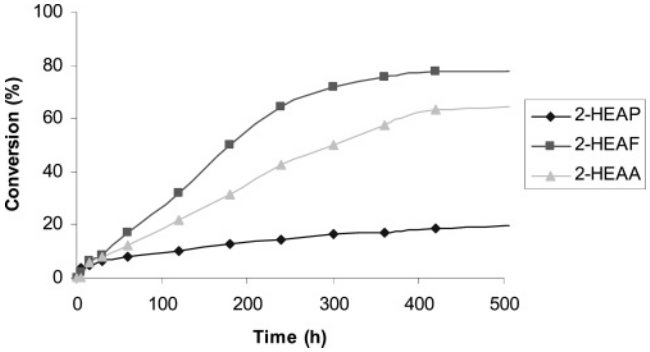



**Figure 8.** Conversion of benzaldehyde in the benzaldehyde−heptanal condensation.

temperature, higher viscosity was observed when the salt was of higher molecular weight. The effect of the temperature is similar for the whole salts.

2. The organic residual chain in the cation forming the ionic liquid has strong effects on the physicochemical properties, with the steric hindrance being a key factor for accommodation into a liquid structure. The ions enclosed are of two types: linear (the anion) and globular (the cation), and the factors studied were the substitution and then the bulk power character. The degree of their influence depends on the nature of cation, but the influence of anion residue is higher[4,5] because of its linear and longer structure. This factor produces a higher disturbation in terms of the accommodation of ions. For these ions, the bulk cation develops lower steric hindrance influence than the linear anion. This fact may be observed in terms of higher values of densities and ultrasonic velocities for those salts of the lighter anion (in each case) and the heavier cation (for the same anion).[5]

3. The influence of molecular structure in terms of conductivity produces the lowest values for 2-HDEAF and 2-HTEAF and the largest for 2-HEAF. The effect of temperature in this magnitude produces a considerable increment toward high values by ion mobility.

4. As observed in Figure 5, the longer the size of the cation (triethylamine cation), the lower the value of isobaric expansibility obtained.

5. On the basis of these experimental observations and as explained above, because of the low cost and simplicity of synthesis, the potential interest of these liquid salts is great due to the possibility of a tailored-designed ionic liquid or ionic liquid mixture, which shows those physicochemical properties more adequate for industrial applications, such as unit operations or cosolvents for catalysis reactions, which are being studied in our laboratories.

6. As observed from the experimental data, the studied solvents used in homogeneous catalysis play a unique role in dissolving and stabilizing the reactants of the studied aldol condensations, but must not react or compete with the reactants. An important feature of homogeneous systems enclosing ionic liquids is that they are highly efficient, and highly specific chemo-, stereo-, regio-, and enantioselectivities can be attained. The disadvantage, however, is the need to separate the solvent and catalyst from the product and unused reactants at the end of the reaction. Ionic liquids offer the opportunity of combining the advantages of both homogeneous and heterogeneous catalysis in one system, because some of them show sharp immiscibility in polar reaction media. The development of applications of three-dimensional heterogeneous catalysis using ionic liquids as supports should present challenges for the next decades. At the present time, several urgent questions regarding basic aspects of ionic liquids need to be addressed. Among them, the physicochemical principles of the liquid properties and solubility of ionic liquids remains a research subject of ionic liquid study today.

## Conclusions

A new protocol for the synthesis of short aliphatic chain ionic liquids has been developed. For this new family of ionic liquids, a series of characterization has been carried out: the temperature dependence of density and the study of ultrasonic velocities and conductivity. Good results were obtained in terms of conversion and selectivity when these ionic liquids were used as catalysts for a series of aldol condensation reactions with interest for the fine chemistry industry.

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