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Synthesis and Physical Properties of Three Protic Ionic Liquids with the Ethylammonium Cation

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Three protic ionic liquids with the ethylammonium cation, 2-hidroxy ethylammonium butanoate (2-HEAB), 2-hidroxy ethylammonium pentanoate (2-HEAP) and 2-hidroxy ethylammonium hexanoate (2-HEAH) were synthesized through acid-base neutralization reactions between ethanolamine and the corresponding organic acid. After purification, the salt formation was confirmed by FT-IR analysis. Thermophysical properties, such as density, refractive index, viscosity, heat capacity and degradation temperatures were experimentally determined. Melting points temperatures could not be determined within the temperature range studied. However, it was confirmed that these melting points are located below 323.15 K. Other thermodynamical properties, such as the thermal expansion coefficient, the molecular volume and the standard entropy were calculated from the experimental data through correlation equations. These results are in accordance with the consideration that the density is inversely proportional to the molecular volume and the density order is 2-HEAB > 2-HEAP > 2-HEAH.

1. Introduction

When the subject is environmental protection, more and more alternatives must be proposed and discussed. Thinking in new ways to protect and to contribute to the preservation of our planet becomes a daily and a hard task to students around the world.

Ionic liquids are organic salts that are liquids at low temperature and form a family of solvents that have found application in many areas of chemical product and process development. There is an increasing use of ionic liquids as engineering liquids for industrial processing. For example, due to their adjustable hydrophobicity and dissolution ability, ionic liquids have been used as effective solvents in extraction processes and gas separations (Brennecke and Maginn, 2003; Zhao, 2006).The interest in ionic liquids has been boosted in recent years due to increasing need for environmentally friendly fluids. The ionic liquid concept brought into the research field a huge number of new compounds whose properties and phase behavior were not only unknown but also, in some aspects, different from what was previously known (Coutinho, 2011). By variation of the anion or the cation, properties such as viscosity, density, and refractive index can be modulated, opening the possibility of tailored ionic liquids designed for industrial applications.

The use of ionic liquids in process and product design requires the knowledge of their thermophysical properties. This knowledge must be as rich as it is required to decide whether the use of ionic liquids could be extended from the laboratory to industrial level. Nevertheless, the scarce knowledge of ionic liquids thermophysical properties is a barrier for their development for industrial applications.

A common practice for design purposes is to oversize equipment. This procedure leads to an increase of plant building and products production cost; on the other hand, lower uncertainties in the available data would lead to a decrease in plant and production costs (Aparicio et al., 2010). Therefore, there is a clear need for systematic ionic liquids thermophysical properties measurements.

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2. Experimental

2.1 Ionic Liquids Synthesis and Purification

The synthesis of protic ionic liquids consists in an acid-basic neutralization reaction. The base, in this case ethanolamine, was added under stirring in a slow dropwise on a glass flask with the acid (butanoic, pentanoic and hexanoic, respectively). An ice bath system was mounted**,** because the reactions showed exothermic character. The reaction products are an ester and a salt of ethanolamine, the ionic liquid itself (Bicak, 2004; Cota et al., 2007; Alvarez et al., 2010). The ionic liquid purification process consists in a strong agitation and slight heating, at 323.15K, for the vaporization of impurities (residual non reacted and water) under vacuum of 20 kPa. Humidity below 0.1% was obtained after this purification process (Alvarez et al., 2010; Iglesias et al. 2010), and the liquids presented a limpid and viscous appearance. The ammonium salt formation was proved in by FT-IR spectroscopy by using a Shimadzu IR Prestige-21.

2.2 Measurements

Refractive indexes were measured using a Mettler-Toledo RE 40D digital refractometer; densities were measured using an Anton Paar DMA- 5000 oscillating U-tube densimeter; and viscosities were measured in a Anton Paar AMVn sphere automatic viscometer, with a number 4.0 capillary and a 3.0 mm sphere.

Melting point and heat capacity were measured using a Mettler-Toledo DSC1 digital scan calorimeter. The analysis gas was nitrogen 4.6 FID, with a flow rate of 50 mL.min^{-1} and aluminum as crucible material. Decomposition temperatures were analyzed using a Shimadzu thermo gravimeter TGA 50H (thermo balance sensitivity: 0.1µg). The inert atmosphere was dry nitrogen, while the heating rate was 10 K. min^{-1}.

3. Results and Discussions

3.1 FT-IR Spectroscopy

The results of the FT-IR analyses were very similar for the three ionic liquids, showing the same bands at same broad. Specially, two bands should be observed to analyze an ammonium salt formation. One band must be within the 3200-2400 cm^{-1} range, corresponding to the typical ammonium structure. The OH stretching vibration is also embedded in this band. The other important band must be centered at 1600 cm^{-1}, and is a combined band of the carbonyl stretching and the N-H plane bending vibrations. Both these bands can be noted at Figure 1. Alvarez et al. (2010) and Iglesias et al. (2010) synthesized different ionic liquids and similar behavior was observed.

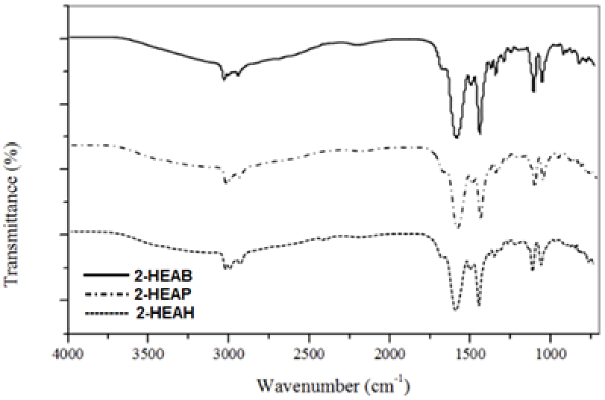

Figure 1. FT-IR Spectra for 2-hidroxy ethylammonium butanoate (2-HEAB), 2-hidroxy ethylammonium pentanoate (2-HEAP) and 2-hidroxy ethylammonium hexanoate (2-HEAH)

3.2 Density, Refractive Index and Viscosity

The experimental density, refractive index and viscosity data are presented as temperature functions in Figures 2, 3 and 4. Complete Tables were not included here due to lack of space. For all ionic liquids, these properties decreased with the temperature increasing. The refractive index results have a considerable decrease, while the viscosity values seems to achieve a limit with temperature increase, almost overlapping the curves. This behavior indicates that all three protic ionic liquids showed an increasing trending packing efficiency with the decreasing of molecular weight, and it is in a good agreement with the results reported by

Alvarez et al. (2010), although Alvarez et al. (2010) worked with different ionic liquids. 2-HEAP at 298 K was the only ionic liquid found on the literature, and the density and refractive index results are in good agreement with those observed by Iglesias et al. (2010).

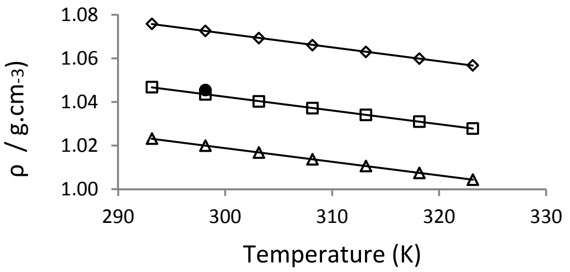

Figure 2. Density: (◊) 2-HEAB, (□) 2-HEAP and (△) 2-HEAH, (●) 2-HEAP literature (Iglesias et al., 2010). The solid lines show the corresponding fit to Equation 1.

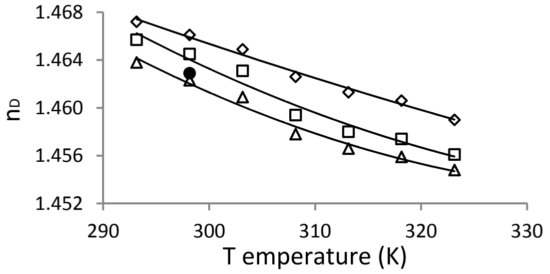

Figure 3. Refractive index: (◊) 2-HEAB, (□) 2-HEAP and (△) 2-HEAH, (●) 2-HEAP literature (Iglesias et al., 2010). The solid lines show the corresponding fit to Equation 1.

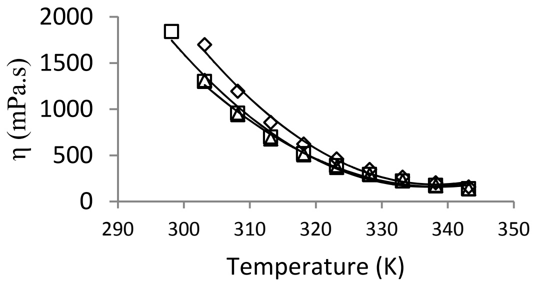

Figure 4.Viscosity of ionic liquids (◊) 2-HEAB, (□) 2-HEAP and (△) 2-HEAH. The solid lines show the corresponding fit to Equation 2.

These experimentally measured density, refractive index and viscosity could be represented as a function of temperature for the three protic ionic liquids, using the correlations (1) and (2).

$$z = AT^2 + BT + C \tag{1}$$

$$\log \mu = A + B/T + C/T^2 \tag{2}$$

Where *z* could be *ρ* or n_D, μ is the viscosity, *T* is the temperature in K and *A*, *B* and *C* are adjustable parameters, shown in Table 1, together with the standard deviations (*σ*). The deviations were calculated by applying equation 3, where *y* is the property studied:

$$\sigma = (\sum_{i}^{n_{DAT}} (y_{exp} - y_{adjust})^2 / n_{DAT})^{1/2} \tag{3}$$

Table 1.Fitting parameters of Equations1 and 2, standard deviations (σ) to correlate the physical properties

Ionic liquids	Physical properties	*A*	*B*	*C*	*Σ*
	ρ/(g. cm^{-3})	$1.000.10^{-6}$	-0.001	1.354	0.001
2-HEAB	n_D	$1.000.10^{-6}$	-0.001	1.640	0.006
	μ/(mPa .s^{-1})	-5.457	2503.180	$3.939.10^4$	7.932
	ρ/(g. cm^{-3})	$6.000.10^{-7}$	-0.001	1.283	0.000
2-HEAP	n_D	$4.000.10^{-6}$	-0.003	1.932	0.020
	μ/(mPa.s^{-1})	-5.224	2457.750	$2.167.10^4$	6.248
	ρ/(g. cm^{-3})	$5.000.10^{-7}$	-0.001	1.254	0.001
2-HEAH	n_D	$4.000.10^{-6}$	-0.003	1.976	0.027
	μ/(mPa.s^{-1})	-5.125	2357.943	$4.260.10^4$	7.528

3.3 Melting Point, Heat Capacity and Degradation Temperature

Ionic liquids calorimetric data are not much broadcast on literature. Any phase transformation, such as a solid melting, could be observed through the analysis of a heat flow versus temperature plot, provided by the differential thermal curve shown in Figure 5. In this kind of plot, baseline changes in sharp peaks indicate component phase changes. Such peaks are formed when the energy supply to the sample and reference start to differentiate from themselves, changing the baseline and tending peak formation. After transition phase the energy supply return to be constant and back to the baseline. In Figure 5, no exothermic peak formation could be observed, which indicates that the melting point was not achieved for any of the three protic ionic liquids within the studied temperature range. The ionic liquid 2-HEAH was the material that showed the larger heat flow variation, but this was still not enough to form a peak and indicate the phase transition. In this way, the melting point for all these protic ionic liquids is located below 253.15 K, although the exact values were not determined.

The heat capacity values are presented on Table 2. The results showed that heat capacity increases with temperature, and also showed that the higher molecular weight ionic liquid has the greater energy storage capacity; thus implies that 2-HEAH requires more energy than the other ionic liquids to increase or decrease its temperature.

Table 2.Heat capacity for2-HEAB, 2-HEAP, 2-HEAH and sapphire (reference material)

T K	2-HEAB $J.g^{-1}.K^{-1}$	2-HEAP $J.g^{-1}.K^{-1}$	2-HEAH $J.g^{-1}.K^{-1}$	Sapphire $J.g^{-1}.K^{-1}$
253.15	1.854	1.861	1.908	0.666
263.15	1.776	1.781	1.890	0.693
273.15	1.727	1.735	1.884	0.718
283.15	1.694	1.708	1.874	0.741
293.15	1.677	1.707	1.877	0.764
303.15	1.682	1.738	1.908	0.785
313.15	1.722	1.814	1.978	0.806
323.15	1.787	1.940	2.082	0.825
333.15	1.884	2.128	2.239	0.843
343.15	2.014	2.395	2.458	0.861
353.15	2.184	2.726	2.758	0.877
363.15	2.346	3.030	3.073	0.892
373.15	2.574	3.320	3.462	0.907

The degradation temperature measurements were performed by TGA analysis. The behavior of all three protic ionic liquids was very similar, as can be seen in the thermogravimetric curves plotted in Figure 6.

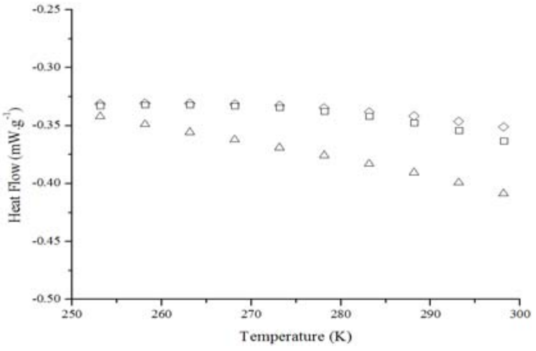

Figure 5. Heat flow versus temperature of ionic liquids (◊) 2-HEAB; (□) 2-HEAP and (▵) 2-HEAH

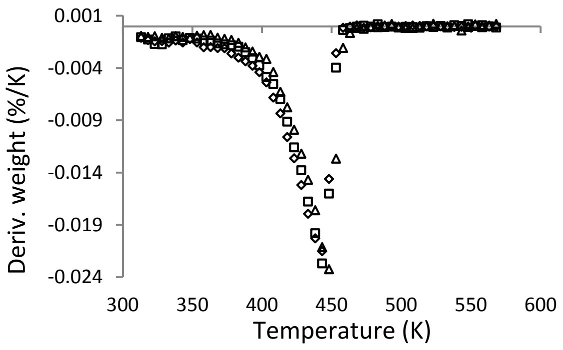

Figure 6.Thermogravimetric curves of ionic liquids (◊) 2-HEAB; (□) 2-HEAP; (▵) 2-HEAH

This behavior shows a poor anion influence on the degradation temperature. Under the conditions of this study, the ionic liquids did not exhibit any detectable mass loss after 340 K. Such very early mass losses are with all probability due to thermally resistant impurities that remained within the samples, even after the purification procedure; considering the extremely hygroscopicity of the ionic liquids, even a small exposition to room temperature conditions can alter the compounds purity. The TGA characteristic temperatures, such as $T_{5\%}$, T_{on} and T_p, are shown in Table 3, and the interval between them is large, as already commented by Ferreira et al. (2012), who verified large increments from initial temperatures to final temperatures of six ionic liquids, although different from ionic liquids of this work.

Table 3. Characteristic temperatures obtained from the TGA curves. $T_{5\%}$ (K): temperature at 5% mass loss; T_{on} (K): extrapolated onset temperature; T_p (K): peak temperature corresponding to the main mass loss stage

Ionic liquid	$T_{5\%}$/K	T_{on}/K	T_p/K
2-HEAB	340.2	376.0	443.1
2-HEAP	347.0	383.0	444.0
2-HEAH	348.1	385.1	448.0

3.4 Thermodynamic Properties

From the experimental measurements, some thermodynamical properties, such as the thermal expansion coefficient and the molecular volume can be correlated as a function of temperature, by using the expressions (4) and (5).

$$\alpha_P = -(1/\rho)\,(\partial\rho/\partial T)_P \tag{4}$$

$$V_{molec}/nm^3 = M/(N.\rho) \tag{5}$$

Here, α_P is the thermal expansion coefficient, ρ is the ionic liquid density and $(\partial\rho/\partial T)_P$ can be obtained from Equation 5 by using the density parameters from Table 4. Also, M is the molar weight, N is the Avogadro number, and V_{molec} is molecular volume of the ionic liquid.

$$(\partial\rho/\partial T)_P = (2\,.A\,.T) + B \tag{6}$$

For all ionic liquids, the variation of the thermal expansion coefficient with temperature is small and can be considered independent of the temperature. Glasser and Jenkins (2004) showed that entropies are reliably linearly correlated with volume per molecule, V_m, thus permitting simple evaluation of standard entropies. For organic liquids, the regression lines generally pass close to the origin, with Equation, 7:

$$S^0/(J.K^{-1}.mol^{-1}) = 1133\,(V_{molec}/nm^3) + 44 \tag{7}$$

The thermal expansion coefficients, the molecular volumes and the standard entropy at 298.15K for all three protic ionic liquids are summarized on Table 4.

Table 4.Thermal expansion coefficients, molecular volumes and standard entropy

	2-HEAB			2-HEAP			2-HEAH		
T K	$\alpha_P.10^4$ K	V_{molec} nm^3	S^0 J.mol^{-1}.K^{-1}	$\alpha_P.10^4$ K	V_{molec} nm^3	S^0 J.mol^{-1}.K^{-1}	$\alpha_P.10^4$ K	V_{molec} nm^3	S^0 J.mol^{-1}.K^{-1}
293.15	5.70	0.230	304.79	6.19	0.259	337.24	5.93	0.283	364.26
303.15	5.55	0.232	306.40	6.12	0.260	339.08	5.87	0.284	366.29
313.15	5.40	0.233	307.94	6.04	0.262	340.83	5.81	0.286	368.26
323.15	5.24	0.234	309.49	5.96	0.264	342.64	5.74	0.288	370.28

4. Conclusions

Three protic ionic liquids with the ethylammonium cation, 2-HEAB, 2-HEAP and 2-HEAH, were synthesized through acid-base neutralization reactions between ethanolamine and the corresponding organic acid. After purification, the salt formation was confirmed by FT-IR analysis. Thermophysical properties, such as density, refractive index, viscosity and heat capacity were experimentally determined.

Melting points could not be determined within the temperature range studied, from 253.15 K to 298.15 K, However, it was confirmed that these melting points are located below 253.15 K. 2-HEAH was the material that showed the greater heat flow variation, but this was still not enough to achieve the melting point. Heat capacity increase with temperature, especially after 308.15K and the higher molecular weight ionic liquid has greater energy storage capacity. The ionic liquids did not exhibit any detectable mass loss after 340 K and the degradation temperature showed poor anion influence. The three ionic liquids showed degradation temperature located above 440 K.

Other thermodynamical properties, such as the thermal expansion coefficient, the molecular volume and the standard entropy were calculated from the experimental data through correlation equations. In all cases the change of the thermal expansion coefficient with temperature is small and then it can be considered independent of the temperature. These results are in accordance with the consideration that the density is inversely proportional to the molecular volume and the density order is 2-HEAB > 2-HEAP > 2-HEAH.

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R.R. Pinto and S. Mattedi would like to dedicate this work to the memory of Professor M. Aznar. Professor Aznar will always be remembered as an example of dedicated, kind and gentle person.

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