ANALYSIS OF DENSITIES AND SURFACE TENSIONS OF BINARY MIXTURES OF IMIDAZOLIUM-BASED IONIC LIQUIDS: INFLUENCE OF CATION AND ANION STRUCTURE OF THE IONIC LIQUID

L. M. Casás, M. R. Currás, M. M. Mato, J. L. Legido and J. García*

Departamento de Física Aplicada, Facultad de Ciencias Experimentales, Universidad de Vigo, Lagoas Marcosende s/n, 36310 Vigo, Spain

*Corresponding author: fafina@uvigo.es.

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Introduction: Ionic liquids (ILs) have an increasing number of industrial applications, for example as alternative absorbents to the conventional working fluids. Furthermore, most of the marketable absorption refrigeration machines are operated with ammonia-water or lithium-water as the working mixtures. However, these working pairs have some important disadvantages, such as the high pressures and the necessity of a rectification column in the generator. In absorption technology a fluid with strong volatility is used as refrigerant, whereas a second fluid with much smaller volatility is used as absorbent.

In fact, Brennecke [1] and Sen and Paolucci [2] propose to use ionic liquids as absorbent with CO_2 as refrigerant. Kim et al. [3] have analyzed as refrigerant-absorbent systems 1-butyl-3-methylimidazolium bromide or 1-butyl-3-methylimidazolium tetrafluoroborate + 2,2,2-trifluoroethanol (TFE), concluding that more properties such as surface tension are required in order to evaluate this kind of mixtures as working pair for heat pumps. Thus, the aim of the present work deals with the necessity of having thermophysical data of mixtures that contain alternative absorbents that are required for the industries of refrigeration and of air conditioning by absorption. Because of that, our group has realized a theoretical and experimental study of several thermophysical properties of mixtures containing TFE as refrigerant and three ionic liquids as absorbents: 1-ethyl-3-methylimidazolium tetrafluoroborate ([e-mim][BF4]), [b-mim][BF4], and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([b-mim][NTf2]) [4-6]. In this study, we present density and surface tension at atmospheric pressure and 308.15 and 318.15 K of these three pure ILs and their mixtures. This work has a double motivation: the first one is focused on the influence of the the size of the cation and the kind of the anion in the density and surface tension and the second one deals with the evaluation of reliability of several pure ILs or mixtures of ILs as novel absorbents for the refrigerantion by absorption.

Experimental section: The samples were prepared by mass using a Mettler AE-240 balance, with a precision of $\pm 5 \cdot 10^{-5}$ g, which leads to an estimated uncertainty in molar fraction of $\pm 10^{-4}$. Densities of pure liquids and their mixtures (ρ) were measured with an Anton Paar DMA 4500 vibrating tube densimeter. The accuracy of this device is $5 \cdot 10^{-5}$

$g \cdot cm^{-3}$. The density measuring cell is thermostated with a temperature stability of 0.01 K. Water and air were used for calibration. Surface tension (σ) was measured using a Lauda TVT2 automated tensiometer with an accuracy of 10^{-1} $mN \cdot m^{-1}$, which is based on the principle of the pending drop volume. This technique consists of measuring the volume of a drop detaching from a capillary with circular cross-section.

Results and Discussion: Data of densities of pure [e-mim][BF4], [b-mim][BF4] and [b-mim][NTf2] ILs are shown in Figure 1. The average absolute relative deviations (ARDs%) for densities between our values and those from literature are lower than 1% [4-6]. In the case of the surface tensions we have found values of this property at 298.15 K but not at 308.15 and 318.15 K. Although our experimental values are in agreement with the values at 298.15 K, showing a trend of surface tension that decreases when the temperature increases.

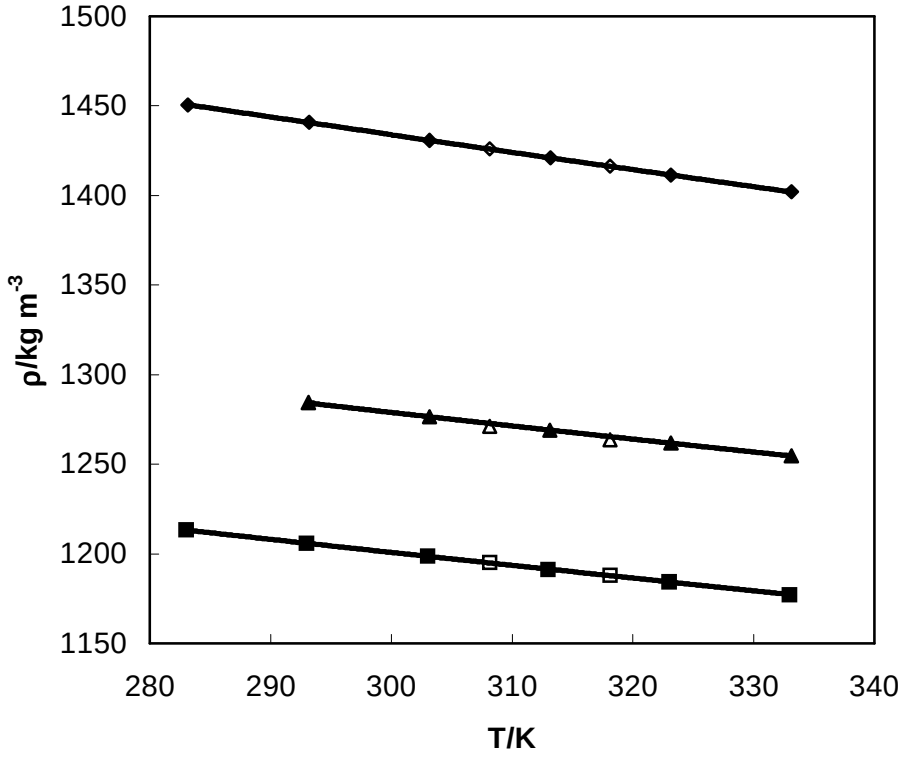

Figure 1. Densities of imidazolium ILs aginst the temperature. Experimental points: (◆,◇)[b-mim][NTf2], (▲, △)[b-mim][BF4], (■, □)[e-mim][BF4]. Black symbols [4-6], white symbols [this work].

Conclusions: At 308.15 and 318.15 K the highest densities and the lowest surface tensions correspond to [b-mim][NTf2]. Thus, this IL could be preferred for the industrial application (refrigeration by absorption) although other properties should be taken into account.

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References:

1. J. F. Brennecke, Ionic liquids for energy applications, *The 37th Great Lakes Regional Meeting*, American Chemical Society, Milwaukee, WI, USA, May 31-June 2, 2006.
2. M. Sen, S. Paolucci, Using carbon dioxide and ionic liquids for absorption refrigeration, *7th IIR Gustav Lorentzen Conference on Natural Working Fluid,* Trondheim, Norway, May 28-31, 2006.
3. K. S. Kim, B.-K. Shin, H. Lee, F. Zielgler, Refractive index and heat capacity of 1-butyl-3-methylimidazolium bromide and 1-butyl-3-methylimidazolium tetrafluoroborate, and vapor pressure of binary systems for 1-butyl-3-methylimidazolium bromide + trifluoroethanol and 1-butyl-3-methylimidazolium tetrafluoroborate + trifluoroethanol *Fluid Phase Equilibria* 218 (2004) 215–220.
4. M. R. Currás, M. F. Costa-Gomes, P. Husson, A. A. H. Padua, J. Garcia, Calorimetric and Volumetric Study on Binary Mixtures 2,2,2-Trifluoroethanol +(1-Butyl-3-methylimidazolium Tetrafluoroborate or 1-Ethyl-3-methylimidazolium Tetrafluoroborate) *Journal of Chemical Engineering Data* 55 (2010) 5504–5512.
5. M. R. Currás, J. Vijande, M. M. Piñeiro, L. Lugo, J. Salgado, J. Garcia Behavior of the Environmentally Compatible Absorbent 1-Butyl-3-methylimidazolium Tetrafluoroborate with 2,2,2-Trifluoroethanol: Experimental Densities at High Pressures and Modeling of PVT and Phase Equilibria Behavior with PC-SAFT EoS *Industrial Engineering Chemical Research* 50 (2011) 4065–4076.
6. M. R. Currás, P. Husson, A. A. H. Padua, M. F. Costa-Gomes and J. Garcia, Experimental densities at high pressures of 1- butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide+2,2,2- trifluoroethanol, *XVII Second Iberian Meeting on Ionic Liquids (2ndIMIL)*, Santiago de Compostela and A Coruña, Spain, July 20-22, 2011.