International Workshop on Ionic Liquids– Seeds for New Engineering Applications

2-3 February 2012, Lisbon, Portugal

THERMAL PROPERTIES OF NEW PHOSPHONIC-BASED IONIC LIQUIDS WITH CARBON NANOTUBES

M.A. Fonseca[1], A.G.M. Ferreira[2], M.S.A. Oliveira[1], and André F. Ferreira[2]

[1]TEMA – Mechanical Engineering Department, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

[2]Department of Chemical Engineering, University of Coimbra, Polo II, Rua Silvio Lima, 3030-970 Coimbra, Portugal

*Corresponding author: abel@eq.uc.pt

Abstract: Different types of phosphonic-based ionic liquids, namely, [P66614][Phos] – CYPHOS 104; [P4441][MTSO] – CYPHOS 108 and [P66614][NTf2] – CYPHOS 109, were evaluated through thermal analysis. The results show that thermal conductivity of these ionic liquids (ILs) are 0.135 W/mK, 0.155W/mK and 0.137 W/mK, at 289K, for CYPHOS 104, CYPHOS 108 and CYPHOS 109, respectively. The addition of multiwalled carbon nanotubes (MWCNT) has shown a slightly increasing in thermal conductivity: from 0.135 to 0.137 W/mK (at 289K) for the CYPHOS 104, and for an addition of 0.05 % vol. of MWCNT. For the CYPHOS 109, it was prepared two ILs with different volume fraction of MWCNTs (0.05% and 0.1%). The results have shown a consistent slightly increasing of the thermal conductivity. It was also observed a decreasing of the thermal conductivity with increasing temperature.

Materials: The Ionic Liquids (ILs) were kindly supplied upon request by CYTEC under the brand name CYPHOS 104 ([P66614][Phos]), CYPHOS 108 ([P4441][MTSO]) and CYPHOS 109 ([P66614][NTf2]). A vacuum of about 1 Pa and moderate temperature (70ºC) were applied to the ILs samples to reduce the water content and volatile species to negligible values. The raw multiwalled carbon nanotubes (MWCNT) were purchased to Shenzehen Nanotech Port Co. Ltd, with the following specifications: diameter of >50 nm and with a length of 10-20 um. The raw MWCNT were chemically treated, through Esumi, *et al.* [1] procedure, in order to ensure an uniform distribution of the MWCNT into IL. The treated MWCNT were added to IL and mixed by a magnetic stirrer for 10-20 minutes for an homogeneous distribution.

Experimental Procedure: The thermal conductivity was measured using a KD2 Pro (Decagon Devices). The measurement principles is based on the hot-wire method. The sensing probe has 1.3 mm diameter and 60 mm long, with an accuracy of 5% from 0.2 – 2 W/mK and ± 0.01 W/(mK) from 0.02 – 0.2 W/mK. The sensing probe is inserted vertically into the sample (~20 ml), which is inserted in a double jacketed bottled. Through the use of this double jacketed bottled it is possible to control the sample temperature by the use of a circulating thermal bath. The thermal conductivity was measured for temperatures ranging from 283 to 353 K. At least 10 measurements were taken at each temperature, with a delay of 15 min.

Results and Discussion: In Figure 1 it is shown the thermal conductivity variation for the studied ILs over the temperature range from 283 to 353 K. The errors bars are not shown due to the relatively small error associated to each point (error bars are smaller than the used symbols). For all studied ILs it was observed a similar trend of the thermal conductivity, which slightly decreases with increasing temperature. The data for the CYPHOS 104 and for CYPHOS 108 clearly shows a linear dependence of the thermal conductivity over the temperature range. The data can be fitted through a linear correlation, $k = mT + b$, being *k* the thermal conductivity (W/mK) and *T* the temperature (K). The fitted parameters, *m* and *b*, are calculated and depicted in Figure 1. The *m* value is very small (-6×10^{-05} W/mK^2 and -9×10^{-5} W/mK^2, for CYPHOS 104 and CYPHOS 109, respectively) indicating the slight dependence of the thermal conductivity with temperature, and the negative sign indicate the decreasing with increasing temperature. Different authors used this simple correlation for other ionic liquids [2,3]. For the CYPHOS IL 109 it is not so clear the linear dependence of the thermal conductivity with the temperature.

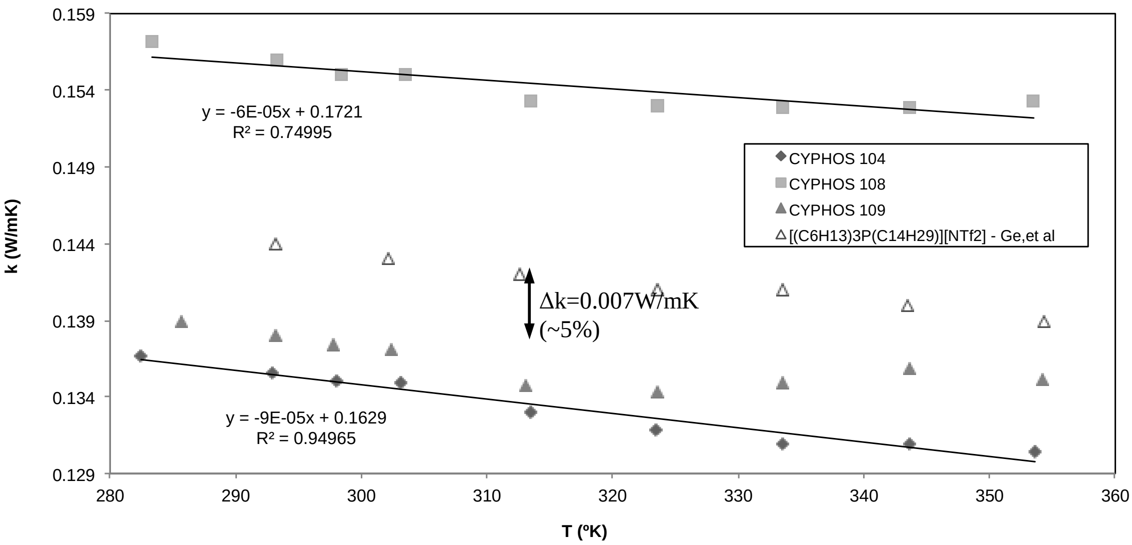

Figure 1. Thermal conductivity for the studied ILs. A comparison is made with values from the bibliography.

At room temperature (RT), the thermal conductivity of the CYPHOS 109 is about 0.138 W/mK, and can be compared with the one observed by Ge, et al. [2]. Although there is a slight divergence of about 0.007W/mK between these values, corresponding to approximately 5%. In Figure 1 it is also made a comparison between the measured thermal conductivity and the one observed by Ge, et al. [2]. This difference can be related with the presence of water in the ionic liquid, which may alter the thermal conductivity. Some authors studied the influence of water content in thermal conductivity, and they observed an enhancement of the thermal conductivity with increasing water content. The slightly decreasing of the thermal conductivity with increasing temperature observed in ionic liquids may be correlated with convection effects that may not be so significant in ILs case, suggesting that convection is not influencing the measured thermal conductivity.

The addition of MWCNT has shown a slight increase in thermal conductivity for the CYPHOS 104 and CYPHOS 109, as shown in Figure 2. Results are consistent with the one observed by Castro, el al [4]. More studies are been made by the group, with other ILs and some practical applications has been evaluated the ILs with CNTs.

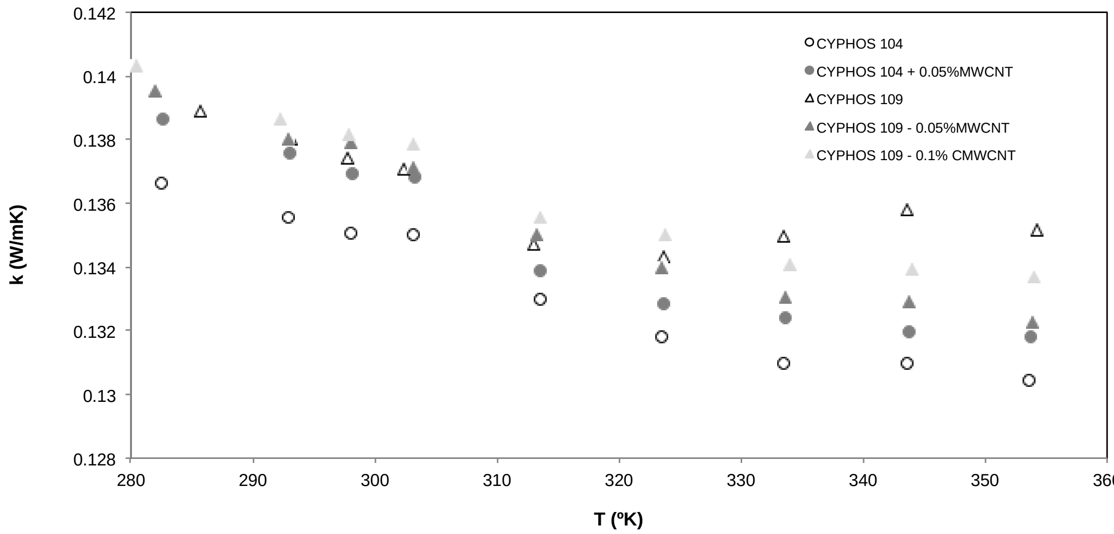

Figure 2. Thermal conductivity of the CYPHOS 104 and CYPHOS 109, pure and with MWCNTs.

Conclusions: The thermal conductivity data obtained have an estimated uncertainty of (about) ±0.001 W/mK and are in good agreement with the scarce available literature data. Moderate enhancements of k (0.5 % to 1 %) were observed for the ionafluids ([P66614][Phos]+0.05 %MWCNT) in the studied range of temperature and these enhancements can be compared with the negligible increase in k which is observed for [P66614][NTf2] even with a loading of 0.1 % of MWCNT. To clarify the behaviour of the phosphonium-based ianofluids, more experimental data will be needed on thermal conductivity of these materials.

References:

1. Esumi, K., Ishigami, M., Nakajima, A., Sawada, K. and Honda, H., *Chemical treatment of carbono nanotubes*, Carbon 34 (1996) 279.
2. Ge, R., Hardacre, C., Nancarrow, P. and Rooney, W., *Thermal conductivity of Ionic Liquids over the temperature range from 293K to 353K*, J. Chem. Eng. Data, 27 (2007) 1819.
3. Valkenburg, M.E. Van, Vaughn, R.L., Williams, M. and Wilkes, J.S., *Thermochemistry of ionic liquid heat-transfer fluids*", Thermochimica Acta 425 (2005) 181.
4. Castro, C.A.N., Lourenço, M.J.V., Ribeiro, A.P.C., Langa, E. and Vieira, S.I.C., *Thermal properties of Ionic Liquids and IoNanofluids of Imidazolium and pyrrolidinium liquids,* J. Chem Eng. Data 55 (2010) 653.