## ISOBARIC HEAT CAPACITY AT HIGH PRESSURE AND VISCOSITY OF A DIPHENYL ETHER + BIPHENYL MIXTURE FOR SOLAR THERMAL ENERGY STORAGE APPLICATION

L. Lugo<sup>1,2</sup>, D. Cabaleiro<sup>2</sup>, M.C. Martín<sup>1</sup>, J.L. Legido<sup>2</sup> and J.J. Segovia<sup>1\*</sup>

<sup>1</sup>Grupo de Investigación TERMOCAL-Termodinámica y Calibración, Universidad de Valladolid, Paseo del Cauce s/n, E-47011 Valladolid, Spain.

<sup>2</sup>Dpto. de Física Aplicada, Facultade de Ciencias, Universidade de Vigo, E-36310 Vigo, Spain

\*Corresponding author: josseg@eis.uva.es

Keywords: Heat capacity, Viscosity, Heat transfer fluid, Pressure.

Introduction: The dependency of fossil fuels has been increased in the industrialized countries for the last centuries. Although there is a strong need to reduce of harmful CO<sub>2</sub> emissions and establishing secure energy supplies [1], the current relatively high cost per kW rated and problems matching the production of electricity to the demand are the major disincentives to the renewable energies. The storage of the energy generated in renewable systems can overcome the intermittency problem, particularly in wind and solar systems, and is a critical factor in the advancement of solar technologies [2]. Thermal energy storage is a natural capability of solar thermal systems and it has received a lot of attention in recent years. In concentrating solar power (CSP) systems, the thermophysical properties of the heat transfer fluid (HTF) are key parameters for enhancing the overall system efficiencies. Among others, developments focus on improvement of thermal storage looking for heat transfer fluid (HTF) with low melting point, high thermal stability and high heat capacity. On this subject, nanofluids, in which nanosized particles are suspended in liquids, have emerged as a potential candidate for the tailoring and production of heat transfer fluids [3-7]. Concerning the base fluid the HTF currently used in large-scale CSP applications is a high temperature synthetic oil in the solar field consisting of an eutectic mixture of biphenyl/diphenyl ether [8]. With the aim to improve the efficiency and reduce the operational cost of the CSP plants, we evaluate as a previous step the properties of base fluids that transfer and store heat currently. Thus, in this study we present experimental viscosities,  $\eta$ , and isobaric heat capacities,  $C_p$ , of the eutectic mixture of diphenyl ether and biphenyl. The study in the liquid phase was carried out analyzing the temperature (293.15-353.15 K) and pressure (0.1-25 MPa) dependences in  $C_p$  and the temperature (288.15-373.15 K) dependence in  $\eta$ .

**Experimental:** A new automated flow calorimeter [9, 10] for the measurement of high accurate isobaric heat capacities over a wide pressure and temperature range is used. The main advantages of this type of technique are great sensitivity, rapid results, good accuracy as well as that there is no vapour space. It is based on the simultaneous heating and cooling of the calorimetric cell to maintain a fixed difference between the inlet and exit temperatures of the circulating fluid at constant flow rate. The measurements of the heat capacity have been performed at five different flows between (3 and 3.5) cm<sup>3</sup>·min<sup>-1</sup>.

The effect due to friction along the tube (because there is a pressure loss and the process is not isobaric) is corrected. The Poiseuille Law has been applied to determine the dissipative energy, which depends on the tube length and diameter, the viscosity of the fluid and the volumetric flow under the calorimeter conditions. The device can measure heat capacities with an estimated total uncertainty better than 0.5%. A rotational Anton Paar Stabinger SVM 3000 device was used to obtain the experimental viscosity and density values against temperature in the liquid phase at atmospheric pressure. This equipment has a cylindrical geometry and it is based on a modified Couette principle to determine viscosity. Moreover it has a density measuring cell that employs the well-known oscillating U-tube principle. Experimental uncertainties of 1% and 0.05% have been estimated for dynamic viscosity and density, respectively.

**Results and discussion:** The isobaric heat capacities are measured from 293.15 to 353.15 K and up to 25 MPa and these values are analyzed together with its temperature and pressure dependences. New viscosity data for that eutectic mixture are reported as a function of the temperature from 288.15 K to 373.15 K. This viscosity temperature dependence is shown in figure 1.



**Figure 1.** Viscosities against temperature for the eutectic mixture of diphenyl ether + biphenyl. (- - -) Vogel-Fulcher-Tammann model.

In addition, a recent fitting equation proposed by us is applied to adjust  $C_p$  values as a function of temperature and pressure, while Vogel-Fulcher-Tammann (VFT), Avramov-Milchev (AM) and MYEGA models were used to modeling viscosity values. The results obtained by VFT equation are also gathered in figure 1, as an example.

**Conclusions:** Viscosities,  $\eta$ , and isobaric heat capacities,  $C_p$ , of the eutectic mixture of diphenyl ether and biphenyl were experimentally determined. The study was carried out in the liquid phase covering a temperature range from 288.15 to 373.15K for viscosity and over a wide temperature and pressure range for  $C_p$ . The VFT model reproduces the temperature dependence of the viscosity with an average deviation of 0.2%.

**Acknowledgements:** This work was supported by the project ENE2009-14644-C02-01 and Ramón y Cajal Grant Program from the Ministerio de Ciencia e Innovación (Spain). The authors are also grateful to the Foundation Iberdrola and the Universities of Valladolid and Vigo for the financial support.

## **References:**

- 1. S.D. Garvey, The dynamics of integrated compressed air renewable energy systems, *Renewable Energy* 39 (2012) 271-292.
- 2. L. Moens, D.M. Blake, D.L. Rudnicki, M.J. Hale, Advanced thermal storage fluids for solar parabolic trough systems, *Journal of Solar Energy Engineering. ASME* 125 (2003) 112-116.
- 3. M.J. Pastoriza-Gallego, L. Lugo, J.L. Legido, M.M. Piñeiro, Thermal conductivity and viscosity measurements of ethylene glycol-based Al<sub>2</sub>O<sub>3</sub> nanofluids, *Nanoscale Research Letters* 6 (2011) 1-11.
- 4. M.J. Pastoriza-Gallego, L. Lugo, J.L. Legido, M.M. Piñeiro, Rheological non-Newtonian behaviour of ethylene glycol-based Fe<sub>2</sub>O<sub>3</sub> nanofluids, *Nanoscale Research Letters* 6 (2011) 560.
- 5. S.M.S. Murshed, K.C. Leong, C. Yang, Thermophysical and electrokinetic properties of nanofluids A critical review, *Applied Thermal Engineering* 28 (2008) 2109-2125.
- 6. S.K. Das, S.U.S. Choi, H.E. Patel, Heat transfer in nanofluids A review, *Heat Transfer Engineering* 27 (2006) 3-19.
- 7. H.-E. Kwak, D. Banerjee, D. Shin, Enhanced sensible heat capacity of molten salt and conventional heat transfer fluid based nanofluid for solar thermal energy storage application, 4<sup>th</sup> International Conference on Energy Sustainability, Phoenix, AZ, United States, May 17-22, 2010.
- 8. J.W. Raade, D. Padowitz, Development of molten salt heat transfer fluid with low melting point and high thermal stability, *Journal of Solar Energy Engineering. ASME* 133 (2011) 031011-031016.
- 9. J.J. Segovia, D. Vega-Maza, C.R. Chamorro, M.C. Martín, High-pressure isobaric heat capacities using a new flow calorimeter, *Journal of Chemical Thermodynamics* 46 (2008) 258-264.
- 10. G.A. Torín-Ollarves, J.J. Segovia, M.C. Martín, M.A. Villamañán, Thermodynamic characterization of the mixture (1-butanol + iso-octane): Densities, viscosities, and isobaric heat capacities at high pressures, *Journal of Chemical Thermodynamics* 44 (2012) 75-83.