Transport coefficients of binary and ternary mixtures of DCMIX project

E. Lapeira, M. M. Bou-Ali

[1]*Mechanical and Manufacturing Department, MGEP Mondragon Goi Eskola Politeknikoa, Loramendi 4 Apdo. 23, 20500 Mondragon, Spain* elapeira@mondragon.edu, mbouali@mondragon.edu

Abstract: We present the thermodiffusion, molecular diffusion and Soret coefficients of several binary and ternary mixtures of DCMIX project. All measurements were carried out at 25ºC and two experimental techniques have been used such as the thermogravitational column technique (TGC) and the Sliding symmetric Tubes technique (SST). In addition the thermophysical properties of analysed mixtures have been determined. The obtained results show the good agreement with other results of literature measured by different experimental techniques.

Key words: *diffusion, thermodiffusion, Soret, DCMIX project.*

1. Introduction

The interest of the analysis of transport properties in mixtures is increasing because if their important role in several natural processes such as oil reservoirs [1], biology [2]–[4]. That´s why binary liquid mixtures have been widely analysed by the scientific community [5]–[11]. As a result of several years' effort, in 2003 the first Benchmark of binary liquid mixtures was published [12] by five European research groups. With ternary mixtures, the difficulty of determining the transport coefficients is higher because the number of unknown coefficients increases considerable. In addition, there are different theories that are not in agreement [13], [14]. Therefore, different groups joined together with the European Space Station (ESA) and started working on a project in order to analyse transport properties in multicomponent mixtures and try to unify a theory. This project called DCMIX is divided into different phases where the aim of each phase is to analyse different ternary mixtures.

The first phase DCMIX 1, analyses hydrocarbons composed of Dodecane, Isobutylbenzene and 1,2,3,4 Tetrahydronaphthalene. Several works of binary mixtures [15]–[18] and ternary mixtures [19]–[24] of this system have been studied. As a result, in 2015 the first Benchmark values of this ternary system were published [25]. The DCMIX 2 is composed of Toluene, Methanol and Cyclohexane. This system is characterized for being critical because in some range of concentrations liquids are not miscible and in addition, there is a sign change of Soret coefficient [26]–[31]. The third system is DCMIX 3 and it analyses aqueous systems of Trithylene Glycol, Water and Ethanol. Binary mixtures of this system have been already measured previously [11], [32]–[37] and molecular diffusion coefficients of the ternary system have been published recently [38]. Finally, in the fourth system it is going to analyse three ternary systems, DCMIX 2 system, Toluene-1,2,3,4 Tetrahydronaphthalene-Fullerene and Polystyrene-toluene-nhexane.

This work presents Difusion, Thermodiffusion and Soret coefficients together with the thermophysical properties of DCMIX 2 and DCMIX 3 systems.

2. Experimental techniques

To determine the transport coefficients, different techniques have been used as the Thermogravitational Column and the Sliding Symmetric Tubes techniques.

2.1. Thermogravitacional Column

The termogravitational technique [39] allows determining the thermodiffusion coefficient by the variation of the concentration with the height of the column Fig. 1, and some thermophysical properties. Instead of trying to avoid convection as in the elemental Soret cell, the thermogravitational technique adds it to the thermodiffusive separation. The applied temperature gradient makes, generally, the denser component migrate to the cold wall due to thermodiffusion and at the same time it is moved to the bottom part of the column due to convection. Therefore, a vertical concentration gradient is established through the height of the gap.

The theory of the thermogravitational column [40] allows relating the stationary separation to the thermodiffusion coefficient, D_T, by the following expression,

$$\Delta c = -\frac{504 L_z D_T \nu}{g \alpha L_x^4} c_0 (1 - c_0) \quad (1)$$

where $\Delta c = -(L_z \partial\rho / \beta\rho\partial z)$ is the mass fraction difference between the top and the bottom of the gap , $\beta = (1/\rho)(\partial\rho/\rho\partial c)$, ν is the kinetic viscosity, $\alpha = -(1/\rho)(\partial\rho/\partial T)$ is the thermal expansion coefficient, c_0 is the mass fraction of the initial mixture and g is the gravity acceleration.

As a result, the thermodiffusion coefficient for binary mixtures can be defined by

$$D_T = -\frac{g L_x^4}{504} \cdot \frac{\alpha}{c_0(1-c_0)\beta\mu} \cdot \frac{\partial\rho}{\partial z} \quad (2)$$

Where, μ is the dynamic viscosity and $c_0(1-c_0)$ is the product of the initial concentrations.

Fig. 1. *Thermogravitational column.*

2.2. Sliding Symmetric Tubes

The Sliding Symmetric Tubes technique [41] enables the determination of the diffusion coefficient. This setup Fig.

2 is composed by several sets that have two identical tubes one in front of the other that can slide. To measure the diffusion, it is introduced the sample inside the tubes with a slight difference of concentration between the top (low concentration) and bottom (high concentration) tubes to avoid instabilities because of convection.

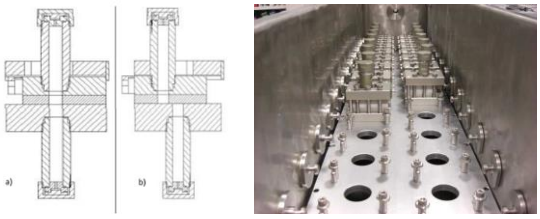

Fig. 2. *a) Tubes in faced position, b) Tubes in separated position, c) Sliding Symmetric Tubes setup.*

To determine the diffusion coefficient, the variation of the concentration of the tubes in square rout of time is analyzed. For binary mixtures, D coefficient can be determined by the following expression,

$$S = \frac{\left(c^{bot} - c^{up}\right)}{H}\sqrt{\frac{D}{\pi}} \qquad (3)$$

3. Results

3.1 DCMIX 2 system

We have measured diffusion, thermodiffusion and Soret coefficients of 26 binary mixtures of DCMIX 2 system in collaboration with the groups of Prof. Köhler in Bayreuth (Germany) and the group of Prof. Shevtsova in Brussels. The results we have obtained in three laboratories by different experimental techniques are in good agreement. In addition, our results are favourable with the ones that have been published in literature.

3.2 DCMIX 3 system

We have determined the thermodiffusion coefficients in the positive range of 12 binary mixtures of DCMIX 3 system, composed by Water-Ethanol and TEG-Water.

Fig. 3 shows the thermodiffusion coefficients of water ethanol binary mixtures in comparison with literature data. There we can observe the sign change at around 70% wt.

In addition, the thermodiffusion coefficient of two ternary mixtures of TEG-Water-Ethanol at (33-33-33 wt %) and (15-25-60 wt %) have been determined by the thermogravitational column technique.

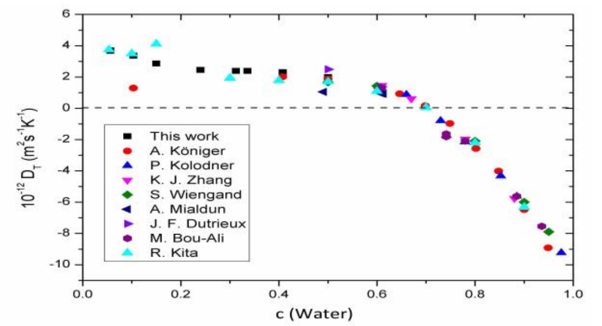

Fig. 3. *Thermodiffusion coefficient of Water-Ethanol binary mixture at 25°C.*

Acknowledgements

The author would like to thank the support of MICRO4FAB, Research Groups (IT009-16) and Research Fellowship (Pre_2014_1_283) of Basque Government and TERDISOMEZ (FIS2014-58950-C2-1-P) of MINECO.

References

[1] F. Montel, "*Importance de la Thermdiffusion en Exploracion et Production Pétrolières*," Entropie, vol. 184/185, pp. 86–93, 1994.

[2] F. J. Bonner and L. O. Sundelöf, "*Thermal diffusion as a mechanism for biological transport.*," Z. Naturforsch. C., vol. 39, no. 6, pp. 656–661, 1984.

[3] A. Bahat and M. Eisenbach, "*Sperm thermotaxis*," Mol. Cell. Endocrinol., vol. 252, no. 1–2, pp. 115–119, 2006.

[4] D. Braun and A. Libchaber, "*Thermal force approach to molecular evolution.*," Phys. Biol., vol. 1, no. 1–2, pp. 1–8, 2004.

[5] W. Köhler and B. Müller, "*Soret and mass diffusion coefficients of toluene/n-hexane mixtures*," J. Chem. Phys., vol. 103, no. 10, p. 4367, 1995.

[6] P. Kolodner, H. Williams, and C. Moe, "*Optical measurement of the Soret coefficient of ethanol/water solutions,*" J. Chem. Phys., vol. 88, no. 10, p. 6512, 1988.

[7] M. Li, W.B. and Segre, P.N. and Gammon, R.W. and Sengers, J.V. and Lamvik, "*Determination of the temperature and concentration dependence of the refractive index of a liquid mixture,*" J. Chem. Phys., vol. 101, no. September, pp. 5058–5069, 1994.

[8] K. J. Zhang, M. E. Briggs, R. W. Gammon, and J. V. Sengers, "*Optical measurement of the Soret coefficient and the diffusion coefficient of liquid mixtures,*" J. Chem. Phys., vol. 104, no. 17, p. 6881, 1996.

[9] M. M. Bou-Ali, O. Ecenarro, J. A. Madariaga, C. M. Santamaría, and J. J. Valencia, "*Thermogravitational measurement of the Soret coefficient of liquid mixtures,*" J. Phys. Condens. Matter, vol. 10, no. 15, pp. 3321–3331, Apr. 1998.

[10] J. J. Bou-Ali, M.M. and Ecenarro, O. and Madariaga, J.A. and Santamaria, C.M. and Valencia, "*Soret Coefficient of Some Binary Liquid Mixtures*," J. Non-Equilibrium Thermodyn., vol. 24, pp. 228--233, 1999.

[11] J. F. Dutrieux, J. K. Platten, G. Chavepeyer, and M. M. Bou-Ali, "*On the measurement of positive soret coefficients*," J. Phys. Chem. B, vol. 106, no. 23, pp. 6104–6114, 2002.

[12] J. K. Platten, M. M. Bou-Ali, P. Costesèque, J. F. Dutrieux, W. Köhler, C. Leppla, S. Wiegand, and G. Wittko, "*Benchmark values for the Soret, thermal diffusion and diffusion coefficients of three binary organic liquid mixtures*," Philos. Mag., vol. 83, no. 17–18, pp. 1965–1971, 2003.

[13] K. Ghorayeb and A. Firoozabadi, "*Molecular, Pressure, and Thermal Diffusion in Nonideal Multicomponent Mixtures*," AIChE J., vol. 46, no. 5, p. 883, 2000.

[14] L. Kempers, "*A thermodynamic theory of the Soret effect in a multicomponent liquid*," J. Chem Phys., vol. 90, p. 6541, 1989.

[15] M. Gebhardt, W. Köhler, A. Mialdun, V. Yasnou, and V. Shevtsova, "*Diffusion, thermal diffusion, and Soret coefficients and optical contrast factors of the binary mixtures of dodecane, isobutylbenzene, and 1,2,3,4-tetrahydronaphthalene,*" J. Chem. Phys., vol. 138, no. 11, 2013.

[16] A. Mialdun and V. Shevtsova, "*Measurement of the Soret and diffusion coefficients for benchmark binary mixtures by means of digital interferometry*," J. Chem. Phys., vol. 134, no. 4, pp. 1–12, 2011.

[17] M. Larrañaga, M. M. Bou-Ali, I. Lizarraga, J. A. Madariaga, and C. Santamaría, "*Soret coefficients of the ternary mixture 1,2,3,4-tetrahydronaphthalene + isobutylbenzene + n-dodecane*," J. Chem. Phys., vol. 143, no. 2, p. 24202, 2015.

[18] G. Wittko and W. Köhler, "*Precise determination of the Soret, thermal diffusion and mass diffusion coefficients of binary mixtures of dodecane, isobutylbenzene and 1,2,3,4-tetrahydronaphthalene by a holographic grating technique*," Philos. Mag., vol. 83, no. 17–18, pp. 1973–1987, 2003.

[19] A. Mialdun, J.-C. Legros, V. Yasnou, V. Sechenyh, and V. Shevtsova, "*Contribution to the benchmark for ternary mixtures: Measurement of the Soret, diffusion and thermodiffusion coefficients in the ternary mixture THN/IBB/nC12 with 0.8/0.1/0.1 mass fractions in ground and orbital laboratories*," Eur. Phys. J. E, vol. 38, no. 4, p. 27, 2015.

[20] M. Gebhardt and W. Köhler, "*Contribution to the benchmark for ternary mixtures: Measurement of the Soret and thermodiffusion coefficients of tetralin+isobutylbenzene+n-dodecane at a composition of (0.8/0.1/0.1) mass fractions by two-color optical beam deflection*," Eur. Phys. J. E, vol. 38, no. 4, p. 24, 2015.

[21] M. Larrañaga, M. M. Bou-Ali, D. A. de Mezquıa, D. A. S. Rees, J. A. Madariaga, C. Santamaría, and J. K. Platten, "*Contribution to the benchmark for ternary mixtures: Determination of Soret coefficients by the thermogravitational and the sliding symmetric tubes techniques*," Eur. Phys. J. E, vol. 38, no. 4, p. 28, 2015.

[22] A. Ahadi and M. Ziad Saghir, "*Contribution to the benchmark for ternary mixtures: Transient analysis in microgravity conditions*," Eur. Phys. J. E, vol. 38, no. 4, p. 25, 2015.

[23] Q. Galand and S. Van Vaerenbergh, "*Contribution to the benchmark for ternary mixtures: Measurement of diffusion and Soret coefficients of ternary system tetrahydronaphtalene-isobutylbenzene-n-dodecane with mass fractions 80-10-10 at 25 °C*," Eur. Phys. J. E, vol. 38, no. 4, p. 26, 2015.

[24] O. A. Khlybov, I. I. Ryzhkov, and T. P. Lyubimova, "*Contribution to the benchmark for ternary mixtures: Measurement of diffusion and Soret coefficients in 1,2,3,4-tetrahydronaphthalene, isobutylbenzene, and dodecane onboard the ISS*," Eur. Phys. J. E, vol. 38, no. 4, p. 29, 2015.

[25] M. M. Bou-Ali, A. Ahadi, D. A. De Mezquia, Q. Galand, M. Gebhardt, O. Khlybov, W. Köhler, M. Larrañaga, J. C. Legros, T. Lyubimova, A. Mialdun, I. Ryzhkov, M. Z. Saghir, V. Shevtsova, and S. Van Varenbergh, "*Benchmark DCMIX1: Soret, thermodiffusion and molecular diffusion coefficients of the ternary mixture THN-IBB-nC12*," Eur. Phys. J. E, vol. 38, pp. 0–6, 2015.

[26] A. Mialdun and V. Shevtsova, "*Temperature dependence of Soret and diffusion coefficients for toluene – cyclohexane mixture measured in convection-free environment .*," AIP - Am. Inst. Phys., vol. 143, p. 224902, 2015.

[27] G. Wittko and W. Köhler, "*Influence of isotopic substitution on the diffusion and thermal diffusion coefficient of binary liquids*," Eur. Phys. J. E, vol. 21, no. 4, pp. 283–291, 2006.

[28] G. Wittko and W. Köhler, "*Universal isotope effect in thermal diffusion of mixtures containing cyclohexane and cyclohexane-d12.*," J. Chem. Phys., vol. 123, no. 1, p. 14506, 2005.

[29] M. M. Bou-Ali, O. Ecenarro, J. a. Madariaga, C. M. Santamaría, and J. J. Valencia, "*Measurement of negative Soret coefficients in a vertical fluid layer with an adverse density gradient*," Phys. Rev. E - Stat. Physics, Plasmas, Fluids, Relat. Interdiscip. Top., vol. 62, no. 1 B, pp. 1420–1423, 2000.

[30] M. J. Story and J. C. R. Turner, "*Flow-cell studies of thermal diffusion in liquids. Part 5. Binary Mixtures of CH3OH with CCl4, Benzene and cyclohexane at 25ºC*," Trans. Faraday Soc., vol. 65, pp. 349–354, 1969.

[31] L. W. Shemilt and R. Nagarajan, "*Liquid diffusivities for the system methanol–toluene*," Can. J. Chem., vol. 45, no. 10, pp. 1143–1148, 1967.

[32] E. Lapeira, M. M. Bou-Ali, J. A. Madariaga, and C. Santamaría, "*Thermodiffusion Coefficients of Water/Ethanol Mixtures for Low Water Mass Fractions*," Microgravity Sci. Technol., 2016.

[33] R. Kita, S. Wiegand, and J. Luettmer-Strathmann, "*Sign change of the Soret coefficient of poly(ethylene oxide) in water/ethanol mixtures observed by thermal diffusion forced Rayleigh scattering*," J. Chem. Phys., vol. 121, no. 8, pp. 3874–3885, 2004.

[34] K. J. Zhang, M. E. Briggs, R. W. Gammon, and J. V. Sengers, "*Optical measurement of the Soret coefficient and the diffusion coefficient of liquid mixtures*," J. Chem. Phys., vol. 104, no. 17, p. 6881, 1996.

[35] S. Wiegand, H. Ning, and H. Kriegs, "*Thermal diffusion forced Rayleigh scattering Setup optimized for aqueous mixtures*," J. Phys. Chem. B, vol. 111, no. 51, pp. 14169–14174, 2007.

[36] A. Königer, B. Meier, and W. Köhler, "*Measurement of the Soret, diffusion, and thermal diffusion coefficients of three binary organic benchmark mixtures and of ethanol–water mixtures using a beam deflection technique*," Philos. Mag., vol. 89, no. 10, pp. 907–923, Apr. 2009.

[37] P. Kolodner, H. Williams, and C. Moe, "*Optical measurement of the Soret coefficient of ethanol/water solutions*," J. Chem. Phys, vol. 88, pp. 6512–6524, 1988.

[38] J. C. Legros, Y. Gaponenko, A. Mialdun, T. Triller, A. Hammon, C. Bauer, W. Köhler, and V. Shevtsova, "*Investigation of Fickian diffusion in the ternary mixtures of water–ethanol–triethylene glycol and its binary pairs*," Phys. Chem. Chem. Phys., vol. 17, no. 41, pp. 27713–27725, 2015.

[39] M. M. Bou-Ali, O. Ecenarro, J. A. Madariaga, C. M. Santamaría, and J. J. Valencia, "*Thermogravitational measurement of the Soret coefficient of liquid mixtures*," J. Phys. Condens. Matter, vol. 10, no. 15, pp. 3321–3331, 1998.

[40] W. H. Furry, R. Clark Jones, and L. . Onsager, "*On The Theory Of Isotope Separation By Thermal Diffusion*," Phys. Rev., vol. 55, pp. 1083–1095, 1939.

[41] D. A. De Mezquia, M. M. Bou-Ali, M. Larrañaga, J. A. Madariaga, and C. Santamaría, "*Determination of Molecular Diffusion Coefficient in n -Alkane Binary Mixtures: Empirical Correlations*," J. Phys. Chem. B, vol. 116, no. 9, pp. 2814–2819, Mar. 2012.