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THERMODIFFUSION COEFFICIENTS OF WATER/ETHANOL MIXTURES FOR LOW WATER MASS FRACTIONS

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Abstract

The difficulty of measuring the thermodiffusion coefficients by optical properties of water-ethanol binary mixtures of approximately 20 wt % of water has been highlighted by several authors in recent years. This is because the concentration derivative of the refractive index $(\partial n/\partial c)_{p,T}$ is near zero at this concentration. For this reason, we measured the thermodiffusion coefficients by means of density analysis using the thermogravitational column technique from 5 wt % to 50 wt % at 25ºC. In addition, we measured the thermophysical properties such as density, dynamic viscosity, thermal expansion and mass expansion.

Keywords: Thermodiffusion, binary mixtures, Soret effect, thermophysical properties, thermogravitational column.

1. Introduction

The presence of a temperature gradient in a mixture creates a separation of the concentration of the components in that mixture. This phenomenon is known as the Ludwig-Soret effect or the thermodifussive effect. The Soret coefficient is used to quantify this phenomenon. In the case of binary mixtures, this coefficient can be obtained by the relationship between the concentration difference Δc, the temperature difference ΔT and the initial concentration of the reference component c_0.

$$S_T = -\frac{1}{c_0\left(1-c_0\right)}\frac{\Delta c}{\Delta T} \qquad (1)$$

In recent years, interest in mass transfer mechanisms in multicomponent mixtures under a temperature gradient has been increasing. This is because of the relevance of this phenomenon in different fields such as biology (Bahat and Eisenbach 2006; Bonner and Sundelöf 1984; Braun and Libchaber 2004), methods of separation (Furry et al. 1939; Platten et al. 2003), optimization of separation processes in microdevices (Martin et al. 2011) and in the petroleum industry (Ghorayeb et al. 2003; Montel 1994).

Over time, several techniques have been developed to analyse this phenomenon. Some of the techniques are used in ground conditions: the Optical Digital Interferometry (Mialdun and Shevtsova 2011), the Optical Beam Deflection (Gebhardt et al. 2013), the Thermal Diffusion Forced Rayleigh Scattering (Wittko and Köhler 2003), the Thermogravitational Column (Bou-Ali et al. 1998) and the Sliding Symmetric Tubes (Larrañaga et al. 2014). In addition, the Selectable Optical Diagnostic Instrument technique (SODI) (Mialdun et al. 2013) is used in microgravity conditions in the International Space Station (ISS) in order to confirm the ground condition results.

In this context, the DCMIX project was established (Diffusion Coefficients Measurements in Ternary Mixtures). The main objective of this project is to study the thermodiffusion effect in multicomponent mixtures. The project is divided into different phases to analyse different ternary mixtures. The first one (DCMIX1), analysed mixtures composed of hydrocarbons such as 1,2,3,4-tetrahydronaphthalene (THN), dodecane (C12) and isobutylbenzene (IBB). The results of one ternary mixture of DCMIX1 were established as a Benchmark (Bou-Ali et al. 2015). The second phase DCMIX2, is measuring mixtures composed of toluene, methanol and cyclohexane. These particular mixtures, are characterized as being critical because in some ranges of concentrations there is an inmiscibility gap and the Soret coefficients are negative (Bou-Ali et al. 2000; Sechenyh et al. 2012; Story and Turner 1969; Wittko and Köhler 2006; Wittko and Köhler 2005). The third phase, DCMIX3, is focused on analysing aqueous mixtures, such as water, ethanol and triethylene-glycol ternary mixtures, and is the subject of this paper.

In the phases DCMIX1, DCMIX2 and DCMIX3, binary mixtures and ternary mixtures were analysed. In fact, in DCMIX1 Larrañaga et al. determined new correlations to predict the thermodiffusion (D_T) and Soret (S_T) coefficient of ternary mixtures from binary mixtures (Larrañaga et al. 2015). In addition, Sechenyh et al. found expressions for the diffusion matrix of a ternary mixture approaching the binary limits (Sechenyh et al. 2015). In DCMIX2, the thermodiffusion, molecular diffusion and Soret coefficients of binary mixtures were analysed (Lapeira et al. 2015)

Each of the abovementioned studies, highlight the importance of analysing the corresponding binary mixtures in each DCMIX phase.

In this work, the analysis of water-ethanol binary mixtures from DCMIX3 is presented. These mixtures have been widely studied in literature by different authors (Dutrieux et al. 2002; Kolodner et al. 1988; Mialdun and Shevtsova 2008; Wiegand et al. 2007; Zhang et al. 1996). In the water-ethanol system the contrast factor $\left(\partial n/\partial c\right)_{p,T}$ is near zero at approximately 20 wt % of water. For this reason, the sensitivity is very low at these concentrations, making it difficult to determine the transport coefficients (S_T, D, D_T) accurately by optical analysis (Kita et al. 2004; Königer et al. 2009).

Due to this problem, we studied the behavior of the thermodiffusion coefficient by means of density analysis of water-ethanol binary mixtures from 5.63 wt % to 50 wt % of water.

This article is organized as follows: in Section 2, the determination of thermophysical properties and the thermodiffusion coefficient measured using the thermogravitational column technique are explained. In Section 3, the results of the thermophysical properties and the thermodiffusion coefficients are shown. Finally, Section 4 outlines the conclusions.

2. Experimental analysis

Determination of thermophysical properties

For the determination of the thermodiffusion coefficient using thermogravitational column technique, it is necessary to know some thermophysical properties such as density, viscosity, thermal expansion and mass expansion.

The preparation of the sample was made with the precision Gram VXI-310 balance with an accuracy of $\pm 0.0001\text{g}$. The denser component was added first, followed by the second component. The density (ρ) was measured by the Anton Paar DMA 5000 density meter with an accuracy of $5\times10^{-3}\ \text{kg}/\text{m}^3$. Thermal expansion $\alpha = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)_{c,p}$ and mass expansion $\beta = \frac{1}{\rho}\left(\frac{\partial\rho}{\partial c}\right)_{T,p}$ coefficients were also analysed using the same density meter. The thermal expansion coefficient was determined by analysing the density of one sample at different temperatures. To measure the mass expansion, we prepared 5 samples with a slight difference of concentration and measured the density of each concentration. Dynamic viscosity (μ) was measured by two devices, the Anton Paar AMVn falling ball microviscometer with an accuracy of $\pm 0.002\text{s}$, and the manual Haake viscometer with an accuracy of $\pm 0.2\text{s}$.

Determination of thermodiffusion coefficient D_T

The thermodiffusion coefficient measurements were performed using the thermogravitational column technique (Bou-Ali et al. 1998). In this technique, a horizontal temperature gradient is applied which creates a vertical separation of the concentration. When the mixture reaches the stationary state, 5 samples are extracted at different heights of the column and the density is measured to determine the concentration distribution (2),

$$\Delta c = \frac{\partial c}{\partial \rho}\frac{\partial \rho}{\partial \text{z}}L_z \qquad (2)$$

Where, $\left(\partial c/\partial\rho\right)_{p,T}$ is defined in a previous calibration, $\left(\partial\rho/\partial \text{z}\right)_{p,T}$ is the variation of the density along the length of the column (Fig. 1) and L_z = (98.0±0.1) cm is the height of the long column.

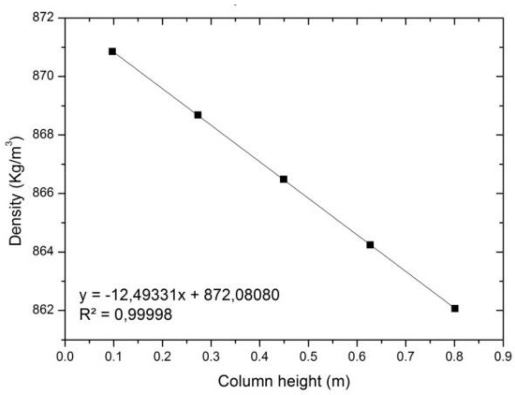

Fig. 1 Variation of density along the length of column of water-ethanol binary mixture at 31.25 wt % of water at steady state.

Finally, having measured the thermophysical properties the thermodiffusion coefficient was determined by the following equation (Bou-Ali et al. 1998),

$$D_T = -\frac{1}{504}\frac{L_x{}^4}{L_z}\frac{1}{c_0(1-c_0)}\frac{\alpha \cdot g \cdot \rho}{\mu}\Delta c \qquad (4)$$

L_x = (0.102±0.0005) cm is the gap of the column, c_0 is the concentration of the reference component and g is the gravity.

3. Results and discussion

There are works in the literature that mention the difficulty of measuring the thermodiffusion coefficients of water-ethanol binary mixtures by analysing the refractive index (Kita et al. 2004; Königer et al. 2009). When the water mass fraction is approximately 20 wt %, the concentration derivative of the refractive index $(\partial n/\partial c)_{p,T}$ undergoes a sign change, and therefore the optical measurement sensitivity is reduced considerably and the errors bars increase.

Consequently, we measured the thermodiffusion coefficient by analysing the density. We deduced that the concentration derivative of the density is highly sensitive in this range of concentrations, see Fig. 2.

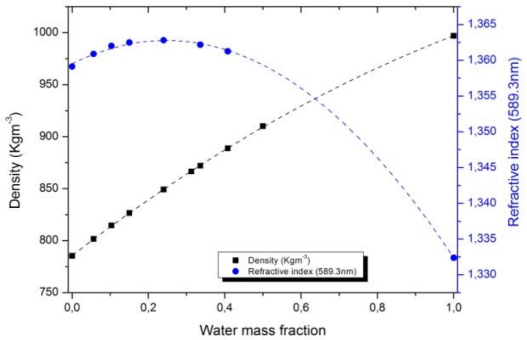

Fig. 2 Density and refractive index (**λ**=589.3nm) of water-ethanol binary mixtures as a function of water mass fraction at 25°C.

The thermodiffusion coefficients we obtained of water-ethanol binary mixtures are compared with the literature data in Fig. 3. There we can observe that there is quite good agreement between values near 50 wt % of water. Nevertheless, for 10.32 wt % of water, there is a marked difference between our results and those of (Königer et al. 2009). This difference might be because the measurements were based on different analysis methods: density analysis in the case of our research and refractive index analysis in the case of Königer

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Table 1 Thermodiffusion coefficients values of analysed binary mixtures at 25ºC.

c water	(10^{-12}) D_T ($m^2s^{-1}K^{-1}$)	ρ ($kg \cdot m^{-3}$)	β	(10^{-3}) α (K^{-1})	μ (mPa·s)
0.0563	3.69 ±0.17	801.815	0.350	1.087	1.184
0.1032	3.28 ±0.13	814.734	0.324	1.077	1.305
0.15	2.94 ±0.11	826.681	0.307	1.061	1.440
0.24	2.46 ±0.08	849.208	0.287	1.025	1.673
0.3125	2.39 ±0.08	866.574	0.273	0.983	1.852
0.336	2.28 ±0.08	872.139	0.271	0.978	1.898
0.4079	2.31 ±0.08	888.821	0.260	0.938	2.040
0.50	1.77 ±0.07	910.085	0.245	0.885	2.134

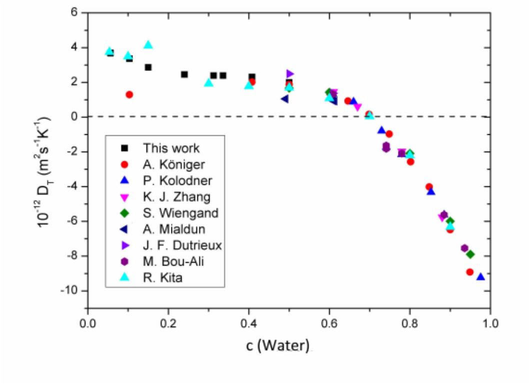

Fig. 3 Thermodiffusion coefficients (D_T) of water/ethanol as a function of mass fraction of water at 25ºC (This work) compared to A. Königer et al. at 25ºC (Königer et al. 2009), P. Kolodner et al. at 25ºC (Kolodner et al. 1988), K. J. Zhang et al. at 25ºC (Zhang et al. 1996), S. Wiegand et al. at 25ºC (Wiegand et al. 2007), A. Mialdun et al. at 22.5ºC (Mialdun and Shevtsova 2008), J. F. Dutrieux et al. at 22.5ºC (Dutrieux et al. 2002), M. M. Bou-Ali 25ºC (Bou-Ali et al. 1999) and R. Kita at 22ºC (Kita et al, 2004).

Table 1 shows the values of all D_T coefficients and thermophysical properties measured at 25ºC. For this specific binary mixture at this range of concentrations, we think it is better to measure using the density analysis.

4. Conclusions

Using the thermogravitational column technique based on density analysis, the present study provides additional values of thermodiffusion coefficients of water-ethanol binary mixtures in the low water mass fraction range.

The results of this work at low water mass fractions have good agreement with the literature data except the 10.32 wt % of water. This might be because the literature values were based on refractive index analysis, while our results were based on density analysis. For this mixture, the sensitivity of the concentration derivative of the refractive index $(\partial n/\partial c)_{p,T}$ is very low thus the authors believe it is more accurate to analyse density instead of refractive index.

Until now, there has been a lack of reliable results in the range of concentrations for low water mass fractions. This research can serve as a base for future studies to determine the DCMIX3 ternary mixtures from binary mixtures.

Acknowledgements

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figure1

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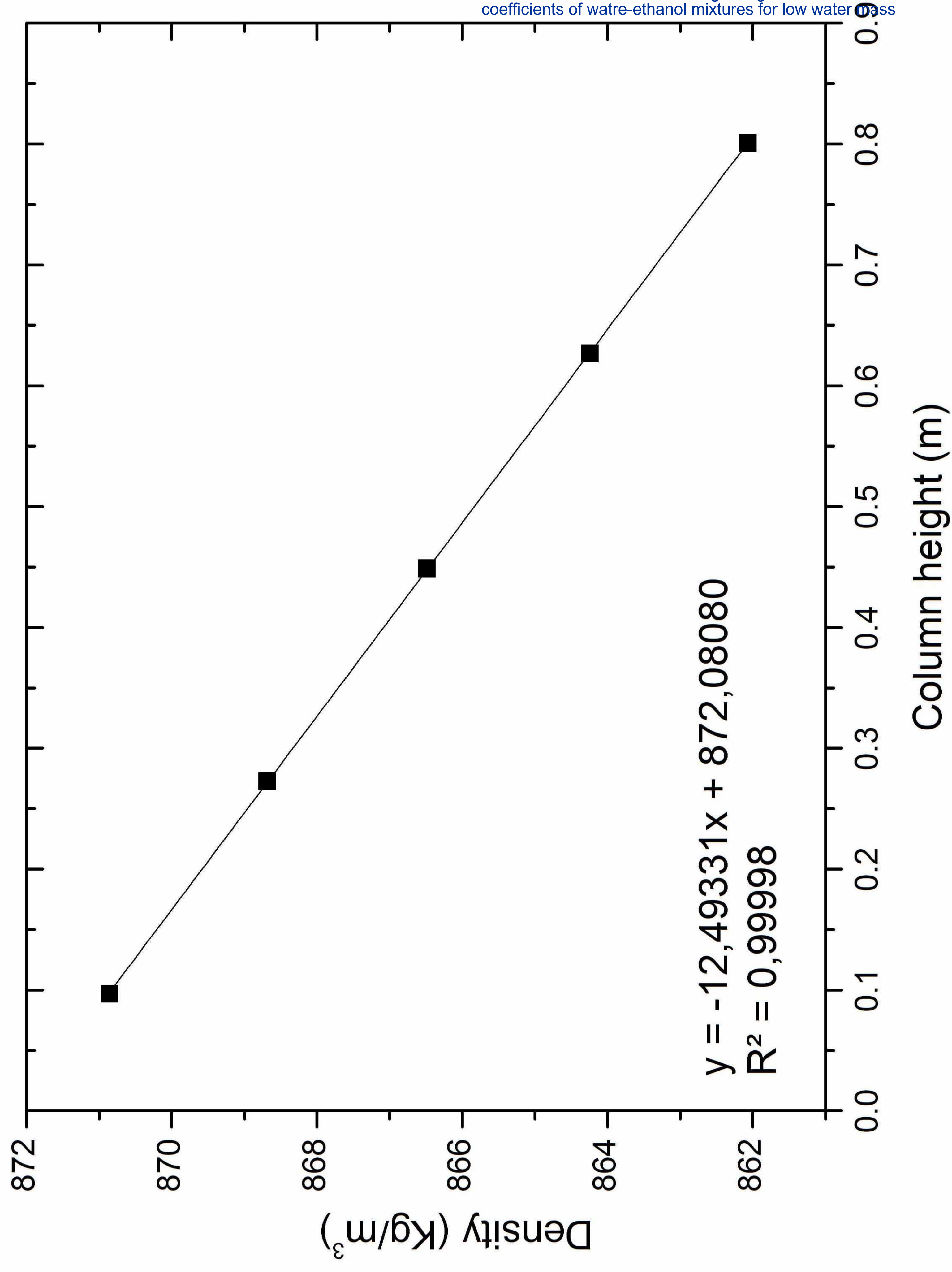


figure2

Click here to download colour figure figure2_thermodiffusion coefficients of watre-ethanol mixtures for low water mass

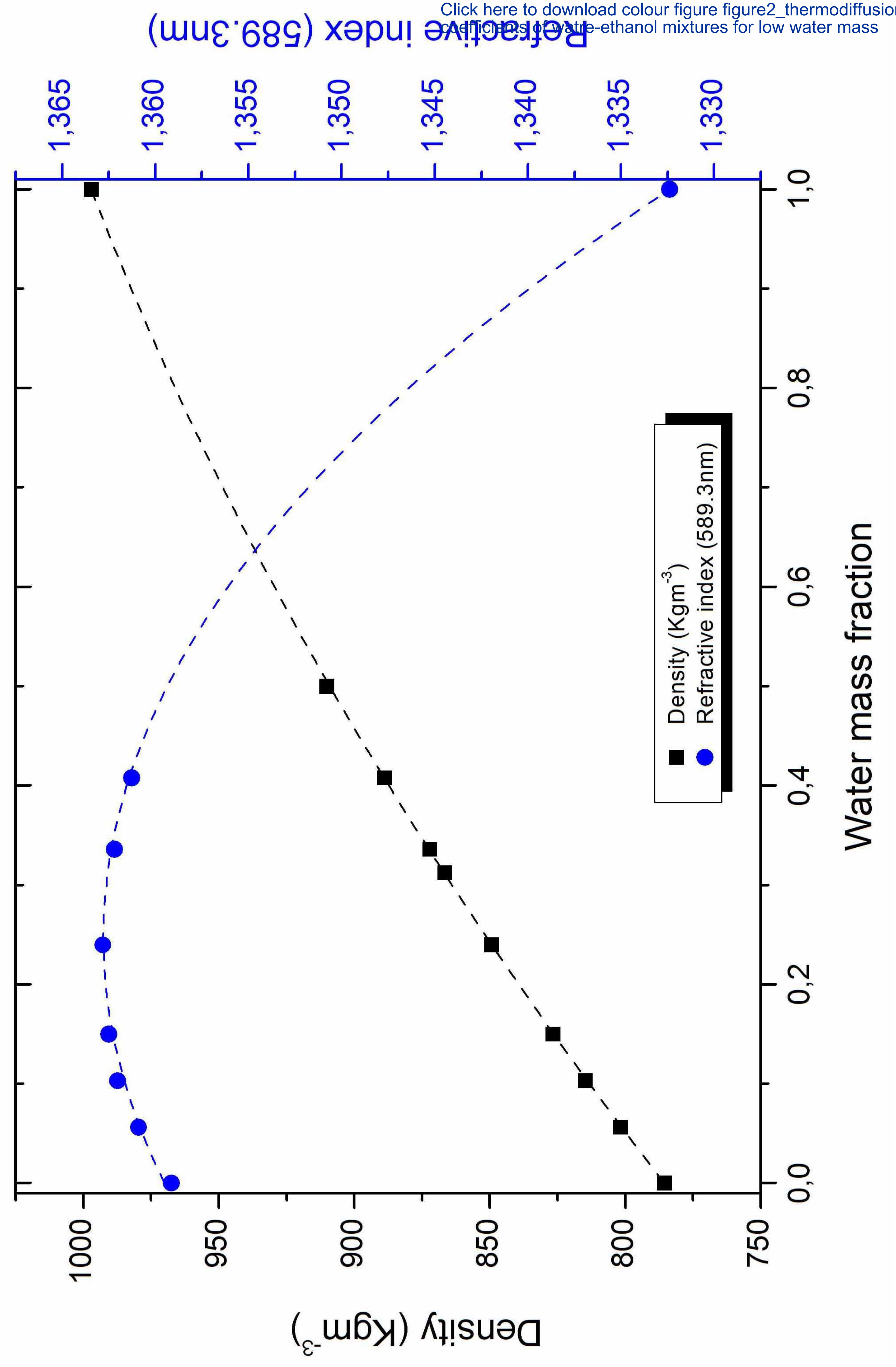
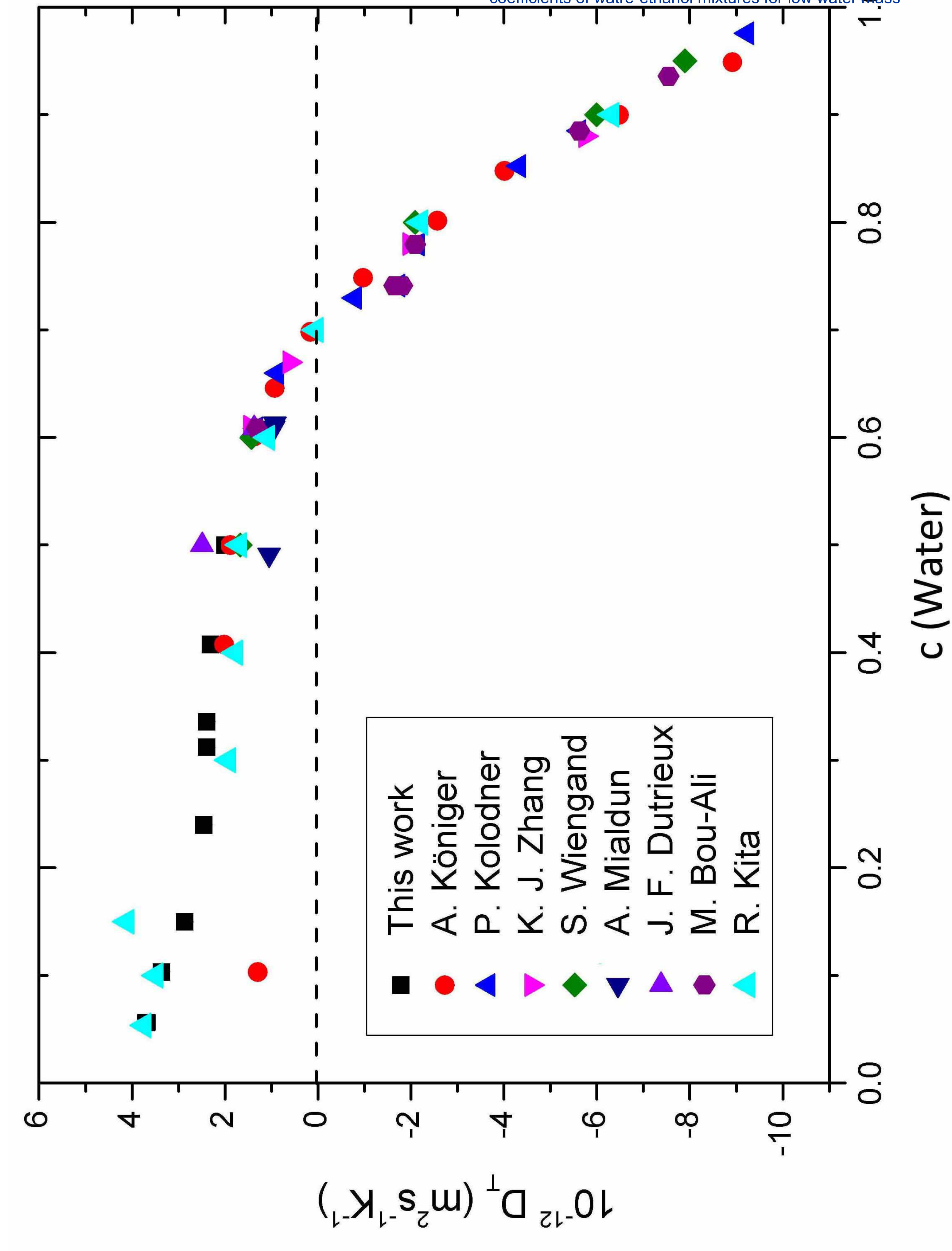


figure3


10^{-12} D_T ($m^2s^{-1}K^{-1}$)
c (Water)
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0.2
0.4
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This work
A. Königer
P. Kolodner
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Determination of thermodiffusion coefficient D_T

The thermodiffusion coefficient measurements were performed using the thermogravitational column technique (Bou-Ali et al. 1998). In this technique, a horizontal temperature gradient is applied which creates a vertical separation of the concentration. When the mixture reaches the stationary state, 5 samples are extracted at different heights of the column and the density is measured to determine the concentration distribution (2),

$$\Delta c = \frac{\partial c}{\partial\rho}\frac{\partial\rho}{\partial \mathrm{z}}L_z \qquad (2)$$

Where, $\left(\partial c/\partial\rho\right)_{p,T}$ is defined in a previous calibration, $\left(\partial\rho/\partial z\right)_{p,T}$ is the variation of the density along the length of the column (Fig. 1) and L_z = (98.0±0.1) cm is the height of the long column.

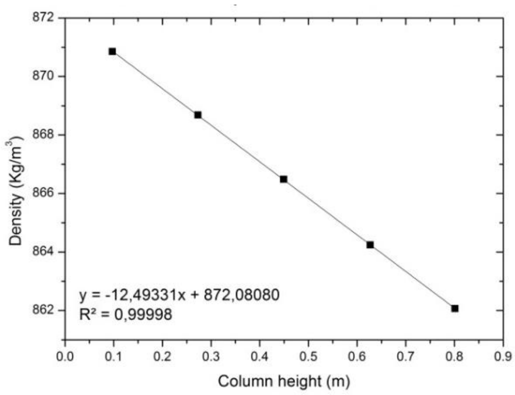

Fig. 1 Variation of density along the length of column of water-ethanol binary mixture at 31.25 wt % of water at steady state.

Finally, having measured the thermophysical properties the thermodiffusion coefficient was determined by the following equation (Bou-Ali et al. 1998),

$$D_T = -\frac{1}{504}\frac{L_x{}^4}{L_z}\frac{1}{c_0(1-c_0)}\frac{\alpha\cdot g\cdot\rho}{\mu}\Delta c \qquad (4)$$

L_x = (0.102±0.0005) cm is the gap of the column, c_0 is the concentration of the reference component and g is the gravity.

3. Results and discussion

There are works in the literature that mention the difficulty of measuring the thermodiffusion coefficients of water-ethanol binary mixtures by analysing the refractive index (Kita et al. 2004; Königer et al. 2009). When the water mass fraction is approximately 20 wt %, the concentration derivative of the refractive index $(\partial n/\partial c)_{p,T}$ undergoes a sign change, and therefore the optical measurement sensitivity is reduced considerably and the errors bars increase.

Consequently, we measured the thermodiffusion coefficient by analysing the density. We deduced that the concentration derivative of the density is highly sensitive in this range of concentrations, see Fig. 2.

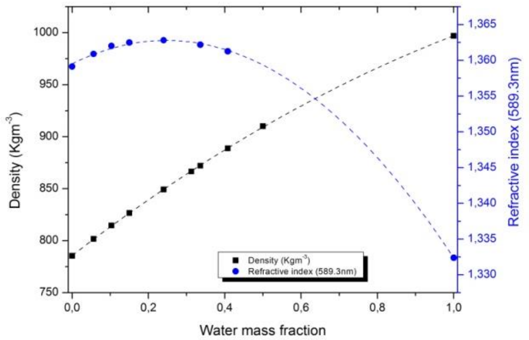

Fig. 2 Density and refractive index (**λ**=589.3nm) of water-ethanol binary mixtures as a function of water mass fraction at 25°C.

The thermodiffusion coefficients we obtained of water-ethanol binary mixtures are compared with the literature data in Fig. 3. There we can observe that there is quite good agreement between values near 50 wt % of water. Nevertheless, for 10.32 wt % of water, there is a marked difference between our results and those of (Königer et al. 2009). This difference might be because the measurements were based on different analysis methods: density analysis in the case of our research and refractive index analysis in the case of Königer

.

Table 1 Thermodiffusion coefficients values of analysed binary mixtures at 25ºC.

c water	(10^{-12}) D_T $(m^2s^{-1}K^{-1})$	ρ $(kg\cdot m^{-3})$	β	(10^{-3}) α (K^{-1})	μ (mPa·s)
0.0563	3.69 ±0.17	801.815	0.350	1.087	1.184
0.1032	3.28 ±0.13	814.734	0.324	1.077	1.305
0.15	2.94 ±0.11	826.681	0.307	1.061	1.440
0.24	2.46 ±0.08	849.208	0.287	1.025	1.673
0.3125	2.39 ±0.08	866.574	0.273	0.983	1.852
0.336	2.28 ±0.08	872.139	0.271	0.978	1.898
0.4079	2.31 ±0.08	888.821	0.260	0.938	2.040
0.50	1.77 ±0.07	910.085	0.245	0.885	2.134

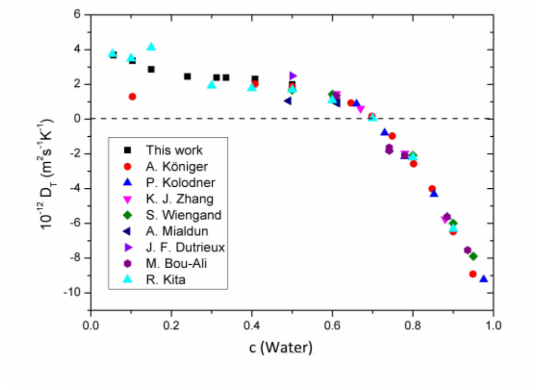

Fig. 3 Thermodiffusion coefficients (D_T) of water/ethanol as a function of mass fraction of water at 25ºC (This work) compared to A. Königer et al. at 25ºC (Königer et al. 2009), P. Kolodner et al. at 25ºC (Kolodner et al. 1988), K. J. Zhang et al. at 25ºC (Zhang et al. 1996), S. Wiegand et al. at 25ºC (Wiegand et al. 2007), A. Mialdun et al. at 22.5ºC (Mialdun and Shevtsova 2008), J. F. Dutrieux et al. at 22.5ºC (Dutrieux et al. 2002), M. M. Bou-Ali 25ºC (Bou-Ali et al. 1999) and R. Kita at 22ºC (Kita et al, 2004).

Table 1 shows the values of all D_T coefficients and thermophysical properties measured at 25ºC. For this specific binary mixture at this range of concentrations, we think it is better to measure using the density analysis.

4. Conclusions

Using the thermogravitational column technique based on density analysis, the present study provides additional values of thermodiffusion coefficients of water-ethanol binary mixtures in the low water mass fraction range.

The results of this work at low water mass fractions have good agreement with the literature data except the 10.32 wt % of water. This might be because the literature values were based on refractive index analysis, while our results were based on density analysis. For this mixture, the sensitivity of the concentration derivative of the refractive index $(\partial n/\partial c)_{p,T}$ is very low thus the authors believe it is more accurate to analyse density instead of refractive index.

Until now, there has been a lack of reliable results in the range of concentrations for low water mass fractions. This research can serve as a base for future studies to determine the DCMIX3 ternary mixtures from binary mixtures.

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