Determination of Soret coefficient for issomasic Dodecane/Hexane and Decane/Pentane binary mixtures under the effect of high pressure

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Summary

The precise measurement of transport properties such as mass diffusion, thermodiffusion coefficients and viscosity in reservoir conditions is essential to complex models predicting and optimizing the exploitation of oil fields. However, available experimental data are very rare at high pressure.

In this work, measurements have been performed on the iso-massic dodecane/hexane (nC$_{12}$-nC_6) and decane/pentane (nC$_{10}$-nC_5) binary mixtures at 25ºC and at high pressure conditions: from 0.1MPa until 20MPa. Thermodiffusion coefficient has been measured by means of thermogravitational technique at Mondragon Goi Eskola Politeknikoa; while diffusion coefficient has been measured by means of Dynamic Near Field Scattering technique at the Université de Pau et des Pays de l'Adour. By a combination of these two measurements, the Soret coefficient of the investigated binary mixture has been established.

Mots clefs : *High pressure, Thermodiffusion coefficient, Molecular diffusion coefficient, Soret coefficient, Binary mixture*

1. Introduction

Soret effect is a transport phenomenon that couples heat and mass fluxes [4]. At constant pressure, in a binary fluid a temperature gradient induces thermal diffusion and a component separation by means of Soret effect. The determination of transport phenomena helps to verify and validate the numerical codes to predict and optimize the exploitation of oil fields. The exploitation of oil fields increasingly requires more knowledge of these properties of hydrocarbon mixtures [5] at high pressure and temperature conditions.

The precise modelling of the distribution of chemical species in oil and gas reservoirs remains a topical issue for the oil industry, especially now that the reserves of fossil fuels are getting more difficult to extract. It is known that due to geothermal gradients and gravitational segregation, transport phenomena takes on importance in the determination of the vertical distribution of species in hydrocarbon reservoirs [1], [6], [7].There is not enough experimental data as well as accurate modelling for binary and ternary mixtures at high pressure. Despite a noticeable experimental progress in the last years, it is not [2], [3], [8].

Due to lack of results, it has been created an international project called SJ10-SCCO. It is an ambitious project that started in 1999 [9], which involves academics (Chinese Academy of Sciences, Imperial College London, Univ. of Mondragon, Complutense Univ., Univ. of Pau and Univ. of Paris-Sud), industrials (RIPED, TOTAL) and the Chinese and European Space Agencies. This project aims at investigating thermodiffusion (Soret effect) of multi-component mixtures of petroleum interest under reservoir conditions. The SJ10-SCCO project is closely related to the DCMIX international project (5 series of experiments to be conducted in SODI in the ISS during 2011-2015) [10]. Three members of the SJ10-SCCO team belong also to the DCMIX project (Dr. Henri Bataller, Prof José Ortiz de Zarate and Prof. Mounir Bou-Ali).

In this present form, the current project is associated with a microgravity experiment (partnership between ESA and China's National Space Science Center) on diffusion/thermodiffusion of fluids of petroleum interest. This experiment has been already launched into space on China´s SJ10 Shi Jian spacecraft.

In this work, we determine thermodiffusion D_T, molecular diffusion D and Soret S_T coefficients of dodecane/hexane (nC$_{12}$-nC_6) and decane/pentane (nC$_{10}$-nC_5) binary mixtures of oil interests at high pressure, 50wt. % and 25 ºC conditions. By a combination of thermogravitational column technique that determines D_T and dynamic near field imaging technique that analyzes D, it has been determined for the first time S_T coefficient at high pressure.

The choice of these two binary mixtures is driven by the need of having more transport phenomena results at high pressure to expand the scientific bibliography for the modelling.

2. Experimental set-up

Thermodiffusion coefficients of both binary mixtures have been measured by means of thermogravitational technique at Mondragon Goi Eskola Politeknikoa; while diffusion coefficient have been measured by means of Dynamic Near Field Imaging technique at the Université de Pau et des Pays de l'Adour. By means of a combination between these two measurements, Soret coefficient have been established for each mixture.

2.1 Thermogravitational column

The thermogravitational column used in this work has cylindrical configuraiton [2]. Stainless steel concentric tubes compose it. In the design of the column, it has considered the validity limits of Furry, Jones and Onsager (FJO) theory [11]. The theory of the thermogravitational columns establishes a relation between the steady state of the mixture inside the system and the thermogravitational coefficient [12]:

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

L_x is the dimension of the gap, g the gravitational acceleration, α thermal expansion coefficient, β mass expansion coefficient, c_0 the mass fraction of the reference component in the initial homogeneous mixture, μ the dynamic viscosity and $\delta\rho/\delta z$ the variation of the density along the height of the column in stationary state.

When the mixture is in steady state, five samples are extracted through five holes distributed equidistantly along the height of the column. These examples are measured in a Anton Paar DMA 5000 densimeter and it is determined the variation of the density in function of the height of the column ($\delta\rho/\delta z$) (Figure 1).

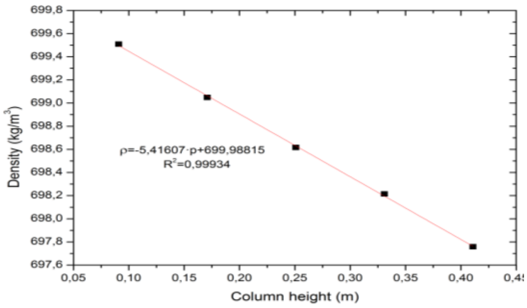

Figure 1. *Variation of density in function of the height of the column for the binary iso-massic nC_{12}-nC_6 mixture at 25 ºC and 60 bar at steady state*

Thermal expansion α as well as mass expansion β properties are determined in a high pressure densimeter. An Anton Paar 512P cell joined to an Anton Paar DMA 5000 densimeter compose this machine. The cell provides harmonic vibration period, which is related to the mass of the mixture, and the densimeter makes visible the data.it is able to work up to 70 MPa.

Figure 2. *High pressure densimeter installation*

In turn, dynamic viscosity (μ) is determined by a commercial HP viscometer (VISCOlab PVT). The device is based in stoke law, in which a piston goes up and down due to magnetic forces induced by two magnetized coils inside a stainless steel body. At the same time, the device takes the timing of each stroke determining m. The viscosity varies considerably with the temperature; hence, the temperature needs to be precisely controlled. Therefore, each experimental test is repeated five times for each mixture and the experimental data is stored and proceeded by VISCOlab PVT Software. The viscometer measures up to 140MPa.

Figura 1. Viscometer (VISCOlab PVT) components

The measurements obtained in function of the pressure show a linear behaviour for the density, dynamic viscosity, thermal expansion and mass expansion. Furthermore, the same comportment demonstrates the thermodiffusion coefficient.

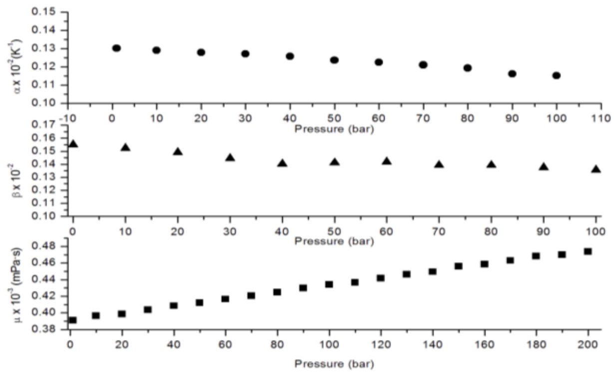

Figure 3. Thermal expansion ●, mass expansion ▲ and dynamic viscosity ■ in function of the pressure for the iso-massic nC_{10}-nC_5 binary mixture at 25ºC

2.2 Dynamic Near Field Imaging

Whenever a temperature gradient is applied to a fluid mixture, thermal and concentration non-equilibrium (NE) fluctuations appear. Theory and experiments have shown that NE fluctuations are long-ranged or non-local and giant [13]. NE fluctuations are strictly related to the transport properties. Analyzing NE fluctuations, one can determine some properties like molecular diffusion coefficient, viscosity or thermal conductivity.

Near Field Imaging is a family of optical techniques [14]–[16] in which the light scattered by an illuminated sample is collected by a pixilated detector together with the (much more intense) transmitted beam in the near field. This way, the refractive index fluctuations that are not visible at the sample plane, are transformed into detectable intensity fluctuations and can be recorded in the form of series of images.

In a binary mixture, the temporal correlation function of NE concentration fluctuations induced by the Soret effect is expected to be a single exponential decay for all wave vectors, with time constants $t_S(q)$ varying as a function of the wave vector q. For wave vectors much larger than characteristic value q_S^*, the decay time is the solutal diffusive one:

$$\tau_S(q) = 1/(Dq^2) \quad \text{Eq. 2}$$

The procedure that follows this technique is to take some pictures to cell that is happening every fluctuations and then, analyze the series of such image maps by Fourier transform. It is applied Differential Dynamic Algorithm [8], [17] to extract the temporal correlation function of NE fluctuations.

3. Results

For a binary hydrocarbon mixture, we can see that the increment of pressure makes decrease the value of the molecular diffusion coefficient (*D*). It has a linear declining tendency. In Figure 4 we can see the molecular diffusion coefficient for the binary nC$_{10}$-nC$_5$ mixture at 25 ºC mean temperature.

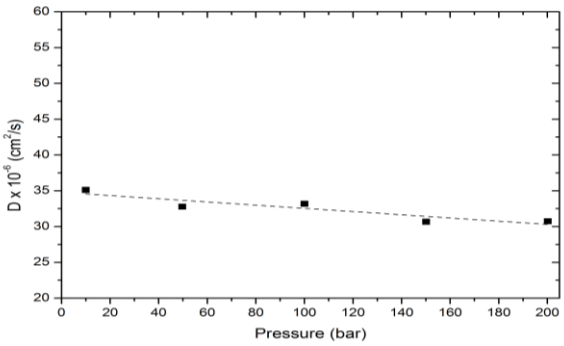

Figure 4. *Molecular diffusion coefficient for nC$_{10}$-nC$_5$ mixture at 25 ºC with the increment of pressure*

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