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# Thermal gravitational separation of ternary mixture *n*-dodecane/isobutylbenzene/tetralin components in a porous medium

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Our present work focuses on the coupling between thermal diffusion and convection in order to improve the thermal gravitational separation of mixture components. The separation phenomenon was studied in a porous medium contained in vertical columns. We performed analytical and numerical simulations to corroborate the experimental measurements of the thermal diffusion coefficients of ternary mixture *n*-dodecane, isobutylbenzene, and tetralin obtained in microgravity in the international space station. Our approach corroborates the existing data published in the literature. The authors show that it is possible to quantify and to optimize the species separation for ternary mixtures. The authors checked, for ternary mixtures, the validity of the “forgotten effect hypothesis” established for binary mixtures by Furry, Jones, and Onsager. Two complete and different analytical resolution methods were used in order to describe the separation in terms of Lewis numbers, the separation ratios, the cross-diffusion coefficients, and the Rayleigh number. The analytical model is based on the parallel flow approximation. In order to validate this model, a numerical simulation was performed using the finite element method. From our new approach to vertical separation columns, new relations for mass fraction gradients and the optimal Rayleigh number for each component of the ternary mixture were obtained.

## I. INTRODUCTION

In the natural world, most materials are found in the form of mixtures of several components and, in most cases, one of the components has particular importance for industry. It is therefore necessary to be able to extract it from the mixture. Thermal gravitational separation is mainly used to separate elements with high added value. Research on the transport properties in multicomponent mixtures is also of great interest to the scientific community (Legros *et al.*;<sup>1</sup> Vafai;<sup>2</sup> Nield and Bejan;<sup>3</sup> Baytas and Pop<sup>4</sup>), because such mixtures are involved in many natural and industrial processes. The case of binary mixtures has been widely studied, see for instance the work of Karimi-Fard *et al.*<sup>5</sup> and Charrier-Mojtabi *et al.*<sup>6</sup> There are several experimental techniques and numerical prediction models that allow the diffusion, thermal diffusion, and Soret coefficients in binary mixtures to be determined accurately, according to Blanco *et al.*<sup>7</sup> Gebhardt *et al.*<sup>8,9</sup> measured the diffusion, thermal diffusion, and Soret coefficients for binary and ternary mixtures. Three different optical techniques were employed, such as optical beam deflection, optical digital interferometry, and thermal diffusion forced Rayleigh scattering. Three-dimensional numerical modeling of Soret-driven convection in a cubic cell filled with a binary mixture of water (90%) and isopropanol (10%) was performed by Shevtsova *et al.*<sup>10</sup> Alonso *et al.*<sup>11</sup> presented results for direct numerical simulations of convection in binary fluids. During the last ten years, many works have been devoted to improving

the experimental device in order to increase separation. Platten *et al.*<sup>12</sup> used a tilted cavity heated from the top. Elhajjar *et al.*<sup>13</sup> studied the unicellular flow appearing at the onset of convection in a binary fluid saturating a horizontal porous cavity heated from below.

Transport properties play an important role in many natural and technological processes and for the fundamental understanding of the behavior of liquids. Nowadays, the focus is on ternary mixtures because it is necessary to analyze and understand them before moving on to multicomponent mixtures. The present work extends the previous studies to ternary mixtures, focusing on the separation of components in a porous enclosure by means of Soret-driven convection. Even today, the Soret effect, a cross effect between temperature and concentration gradients, is poorly understood in multicomponent mixtures. The mass diffusion flux,  $\mathbf{J}_i^d$ , can be induced by both a temperature and a mass fraction gradient. Considering the linear laws of irreversible thermodynamics, the mass flux equations for the components 1 and 2 in a ternary mixture may be written as

$$\mathbf{J}_1^d = -\rho D_{11} \nabla C_1^d - \rho D_{12} \nabla C_2^d - \rho D'_{T,1} \nabla T^d, \quad (1a)$$

$$\mathbf{J}_2^d = -\rho D_{22} \nabla C_2^d - \rho D_{21} \nabla C_1^d - \rho D'_{T,2} \nabla T^d, \quad (1b)$$

where  $D_{11}$ ,  $D_{12}$ ,  $D_{21}$ , and  $D_{22}$  are the molecular diffusion coefficients,  $D'_{T,1}$  and  $D'_{T,2}$  are the thermal diffusion coefficients,  $C_1^d$  and  $C_2^d$  are the mass fraction, and  $T^d$  is the dimensional temperature. The third mass diffusion flux,  $\mathbf{J}_3^d$ , is defined from the condition that the fluxes of all the components must sum to zero.

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In the present work, we extend the previous studies to ternary mixtures focusing on the species separation in a porous cell filled with a ternary mixture. The analytical model presented for the unicellular flow is based on the parallel flow approximation. The separation is expressed in terms of the thermal Rayleigh number ( $Ra$ ), the Lewis number ( $Le$ ), the separation ratio ( $\psi$ ), the cross-diffusion coefficients ( $Cr$ ), and the aspect ratio of the enclosure ( $A$ ). The separation can be optimized in terms of the temperature difference or the cell thickness.

In this work, the results obtained and conclusions drawn are shown in order to serve as a reference for future techniques and measurements, as well as for the setting up and development of new prediction models based on molecular dynamics or on non-equilibrium thermodynamics.

## II. MATHEMATICAL FORMULATION

In this part of the study, we consider a rectangular cavity with an aspect ratio  $A = H/e$ , where  $H$  represents the height of the cavity and  $e$  its thickness. It is assumed that the whole convective phenomenon is perfectly two-dimensional in the  $(x, y)$  plane ( $x$  according to the cell thickness and  $y$  to the height). The cavity is filled with a vertical layer of a porous medium, saturated by a ternary mixture,  $n$ -dodecane/isobutylbenzene/tetralin ( $nC_{12}$ -IBB-THN). The Soret effect and cross-diffusion are taken into account. The cavity is placed between four impermeable walls. The vertical walls are maintained at uniform temperatures, while the horizontal walls are thermally isolated. All the walls are considered to be stiff and the porous layer is taken to be homogeneous and isotropic. It is assumed that Darcy's law is valid and that the Oberbeck-Boussinesq approximation is applicable. The thermophysical properties of the fluid are considered constant except the density in the buoyancy term which varies linearly with the local temperature and mass fractions,

$$\rho = \rho_0 \left( 1 - \beta_T(T^d - T_0) - \sum_{k=1}^2 \beta_{C_k}(C_k^d - C_{0k}) \right), \quad (2)$$

where  $\beta_T$  and  $\beta_{C_k}$  are the thermal and the mass fraction expansion coefficient for each component, respectively.  $T_0$  and  $C_{0k}$  are, respectively, the reference temperature and the initial or reference mass fraction of each component.

The convective flow and the heat and mass transfer are governed by the resulting dimensionless equations,

$$\nabla \cdot \mathbf{V} = 0, \quad (3a)$$

$$\mathbf{V} = -\nabla P + Ra \left( T + \sum_{k=1}^2 \psi_k C_k \right) \mathbf{e}_y, \quad (3b)$$

$$\frac{\partial T}{\partial t} + \mathbf{V} \cdot \nabla T = \nabla^2 T, \quad (3c)$$

$$\varepsilon \frac{\partial C_k}{\partial t} + (\mathbf{V} \cdot \nabla) C_k = \frac{1}{Le_k} \left( \nabla^2 C_k - \nabla^2 T + \sum_{\substack{k=1 \\ j \neq k}}^2 Cr_{kj} \nabla^2 C_j \right). \quad (3d)$$

The reference scales are  $e$  for the geometric parameter,  $(\rho c_p)^* e^2 / \lambda$  for the time, where  $\lambda$  is the thermal conductivity of the saturated porous medium plus the liquid inside the pores, and  $(\rho c_p)^*$  is the heat capacity of the saturated porous medium; it is described as  $(\rho c_p)^* = \varepsilon^* (\rho c_p)_f + (1 - \varepsilon^*) (\rho c_p)_s$ , where  $(\rho c_p)_s$  represents the heat capacity of the porous material,  $(\rho c_p)_f$  the mixture heat capacity, and  $\varepsilon^*$  the cell porosity. Furthermore,  $e(\rho c_p)_f / \lambda$  is the reference scale for the velocity,  $K(\rho c_p)_f / (\lambda \mu)$  for the pressure, and  $T = (T^d - T_0) / \Delta T$  for the temperature, where  $\Delta T = T_1 - T_0$  with  $T_1 \neq T_0$ , and  $C_k = (C_k^d - C_{0k}) / \Delta C_k$  for the mass fraction where  $\Delta C_k = -\Delta T D'_{T_k} / D_{kk}$  where  $D'_{T_k}$  and  $D_{kk}$  are the thermal diffusion coefficient and the mass diffusion coefficient, respectively, for each component.  $D'_{T_k} = F(C_k) D_{T_k}$ , when  $F(C_k)$  is a function verifying  $F(C_k = 0) = 0$  and  $F(C_k = 1) = 0$  (Costesèque *et al.*<sup>14</sup>). Most authors have employed  $F(C_k) = C_k(1 - C_k)$  but Larre *et al.*<sup>15</sup> or Ghorayeb and Firoozabadi<sup>16</sup> used other phenomenological forms. A small variation of  $C_k$  is assumed and  $F(C_k)$  is approximated by  $F(C_{0k})$ , where  $C_{0k}$  is the initial mass fraction corresponding to each component. The problem under consideration now depends on dimensionless parameters such as the thermal Rayleigh number ( $Ra = KHg\beta_T\Delta T / (\nu\alpha)$ , where  $\alpha = \lambda / (\rho c_p)_f$  is the equivalent thermal diffusivity), the separation ratio ( $\psi_k = -(\beta_{C_k} / \beta_T)(D'_{T_k} / D_{kk})F(C_{0k})$ ), the Lewis number ( $Le_k = \alpha / D_{kk}$ ), the cross-diffusion numbers ( $Cr_{kj} = (D_{kj} / D_{kk})(\Delta C_j / \Delta C_k)$ ; Larre<sup>17</sup>), the normalized porosity ( $\varepsilon = ((\rho c_p)_f / (\rho c_p)^*) \varepsilon^*$ ), and the aspect ratio ( $A = H/e$ ).

Through the dimensionless formulation, the porosity occurs explicitly only in (3d). However, it acts across the filtration velocity vector ( $\mathbf{V}$ ), the mass diffusion coefficients ( $D$ ), and the thermal diffusion coefficients ( $D_T$ ). Indeed, the filtration velocity represents the mean fluid velocity taken over an Elementary Representative Volume (ERV). This value is defined by the product of the medium porosity and the interstitial velocity vector ( $\mathbf{V} = \varepsilon \mathbf{V}_f$ ). In addition, tortuosity ( $\tau$ ) affects the coefficients characterizing any transport phenomena and it can be realistically defined (Costesèque *et al.*<sup>18</sup>), for molecular diffusion phenomena by  $\tau^2 = D_f / D$  (Fick Diffusion) or  $\tau_T^2 = D_{T_f} / D_T$  (thermal diffusion), where  $D_f$  and  $D_{T_f}$  represent, respectively, the mass diffusion and the thermal diffusion of the mixture.

The dimensionless boundary conditions of the problem are

$$\mathbf{V} \cdot \mathbf{n} = 0, \quad \forall M_{(x,y)} \in \partial\Omega, \quad (4a)$$

$$\mathbf{J}_k \cdot \mathbf{n} = 0, \quad \forall M_{(x,y)} \in \partial\Omega \quad \forall k = 1, 2, \quad (4b)$$

$$T(0, y) = 1 \quad T(1, y) = 0, \quad (4c)$$

$$\frac{\partial T}{\partial y} \Big|_{x,y=0} = 0 \quad \frac{\partial T}{\partial y} \Big|_{x,y=A} = 0, \quad (4d)$$

with  $\mathbf{J}_k = \nabla C_k - \xi_k \nabla T$ ; for  $\xi_k = (1 - Cr_{kj}) / (1 - Cr_{kj} Cr_{jk})$ .  $\partial\Omega$  characterizes the enclosure borders.

## III. ANALYTICAL SOLUTION

### A. Parallel flow

For the analytical solution, component 1 is the  $n$ -dodecane ( $nC_{12}$ ) and component 2 is the tetralin (THN). The study takes

place far enough from the horizontal walls, so the parallel flow hypothesis (PFH) is verified and side effects do not have to be considered. The analytical study is made in the steady state. The basic flow is given by

$$\mathbf{V} = v(x)\mathbf{e}_y, \quad (5a)$$

$$T(x) = ax + b \quad \forall a \neq 0, \quad (5b)$$

$$C_k(x, y) = m_k y + f_k(x) \quad \forall k = 1, 2. \quad (5c)$$

$m_k$  is a constant that expresses the vertical gradient of the mass fraction of species  $k$  between the two horizontal extremities of the cell. The PFH approximation is not valid close to the horizontal walls. For the absence of boundary conditions to be justified, each component in the cavity is assumed to be conserved and the mass flow rate through a horizontal cross section is equal to zero,

$$\int_0^1 \int_0^A C_k(x, y) dy dx = 0, \quad \forall k = 1, 2, \quad (6a)$$

$$\int_0^1 v(x) dx = 0. \quad (6b)$$

The horizontal boundary conditions of the convective movement for  $x = 0, 1$  are, by continuity

$$\frac{dv}{dx} = Ra \frac{d}{dx}(T + \psi_1 C_1 + \psi_2 C_2). \quad (7)$$

Using the basic unicellular flow (5) and Eqs. (3), an equation system for  $v(x)$ ,  $T(x)$ , and  $f_k(x)$  is found, as

$$\frac{d^2 T}{dx^2} = 0, \quad (8a)$$

$$\frac{d^2 v}{dx^2} - \eta v(x) = 0, \quad (8b)$$

$$\frac{d^2 C_k}{dx^2} = \gamma_k v(x) \quad \forall k = 1, 2, \quad (8c)$$

for

$$\eta = Ra \sum_{k=1}^2 \psi_k \gamma_k, \quad (9a)$$

$$\gamma_k = \frac{Le_k m_k - Le_j m_j Cr_{kj}}{1 - Cr_{kj} Cr_{jk}}. \quad (9b)$$

Using the boundary conditions (4), (6), and (7), the system of equations, which is dependent on the velocity, the temperature, and the mass fractions is solved. The temperature evolution is of the form

$$T(x) = 1 - x. \quad (10)$$

The solutions are given by the following expressions according to the sign of  $\eta$ .

- If  $\eta > 0$ , then  $\eta = \omega^2$ ,

$$v(x) = \sigma \left[ \frac{1 - ch(\omega)}{sh(\omega)} ch(\omega x) + sh(\omega x) \right], \quad (11a)$$

$$f_k(x) = \frac{\gamma_k \sigma}{\omega^2} \left[ \frac{1 - ch(\omega)}{sh(\omega)} ch(\omega x) + sh(\omega x) \right] + \frac{\gamma_k \sigma}{\omega} \left( \frac{1}{2} - x \right) - \xi_k x + \frac{\xi_k - m_k A}{2}. \quad (11b)$$

- If  $\eta < 0$ , then  $\eta = (i\omega)^2$ ,

$$v(x) = \sigma \left[ \frac{cos(\omega) - 1}{sin(\omega)} cos(\omega x) + sin(\omega x) \right], \quad (12a)$$

$$f_k(x) = -\frac{\gamma_k \sigma}{\omega^2} \left[ \frac{cos(\omega) - 1}{sin(\omega)} cos(\omega x) + sin(\omega x) \right] - \frac{\gamma_k \sigma}{\omega} \left( \frac{1}{2} - x \right) - \xi_k x + \frac{\xi_k - m_k A}{2}, \quad (12b)$$

where  $\sigma = -\frac{Ra}{\omega} \left( 1 + \sum_{k=1}^2 \psi_k \xi_k \right)$ .

Figure 1 shows the graphs plotting the evolution of the vertical velocity through the thickness of the cavity in the two cases presented (Figures 1(a) and 1(b)).

The values of physical quantities defining the ternary mixture of *n*-dodecane/isobutylbenzene/tetralin at equal mass fraction proportions, such as the thermal expansion coefficient, the solutal expansion coefficient of *n*C<sub>12</sub> and THN species, and the density and dynamic viscosity of the mixture were determined as in the publication of Leahy-Dios *et al.*<sup>19</sup> The value of the thermal diffusivity of the mixture in the porous medium was calculated from the thermal conductivity of the porous medium and the mixture heat capacity values (Jaber<sup>20</sup>).

The values of the thermal diffusion coefficient and the Soret coefficient of each component of the ternary mixture *n*C<sub>12</sub>-THN-IBB (0.33-0.33-0.33) were defined as described by Gebhardt and Köhler.<sup>9</sup> The values of *n*C<sub>12</sub> and THN mass diffusion coefficients were measured by Larrañaga *et al.*<sup>21</sup> All these values of the physical parameters characterizing the ternary mixture saturating the porous medium under consideration were used to numerically

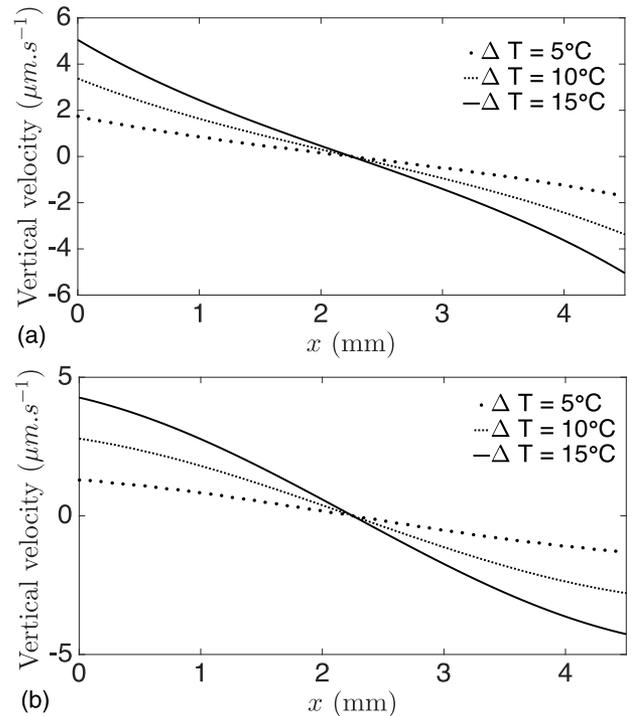


FIG. 1. Vertical velocity evolution according to the cell thickness in both cases (a)  $\eta > 0$  and (b)  $\eta < 0$  for  $\psi_1 = 0.256$ ,  $\psi_2 = 0.144$ ,  $Le_1 = 516.9$ ,  $Le_2 = 304.2$ ,  $Cr_{12} = -0.013$ , and  $Cr_{21} = -0.704$ .

define the dimensionless numbers employed in the analytical solution: the Rayleigh number, the separation ratio, the Lewis number, and the cross-diffusion coefficients.

In order to determine the mass fraction gradient of the two components  $m_1$  and  $m_2$ , it is assumed that the mass fraction flow rate of the components through a horizontal cross-section is equal to zero. This adds two new conditions

$$\int_0^1 (VC_1 + J_1) \cdot e_y dx = 0, \quad (13a)$$

$$\int_0^1 (VC_2 + J_2) \cdot e_y dx = 0, \quad (13b)$$

that give the two following coupled equations:

$$m_1 = \int_0^1 v(x) f_1(x) Le_1 dx - Cr_{12} m_2, \quad (14a)$$

$$m_2 = \int_0^1 v(x) f_2(x) Le_2 dx - Cr_{21} m_1. \quad (14b)$$

These Eqs. (14) are solved according to the temperature difference  $\Delta T$  between the two vertical walls for the case of a ternary mixture whose cross-diagonal elements of the mass diffusion matrix are considered void ( $Cr_{12} = Cr_{21} = 0$ ), and in the case of the real mixture by taking the cross-diffusion effect into account. Note that a mass fraction gradient dimensional shape can be given as follows:

$$m_k^d = -\frac{D_{T_k}}{D_{kk}} \frac{\Delta T}{e} m_k. \quad (15)$$

Table I shows the digital values of the mass fraction gradients ( $m_k^d$ ) of nC<sub>12</sub> and THN according to the temperature difference. We see that when  $\Delta T$  is higher than 15 °C, the mass fraction gradient values of each component are very close in both studies (cross-diffusion omitted and kept).

Furthermore, mass fraction gradients of the components 1 and 2 are drawn according to the temperature difference  $\Delta T$  for the two study cases in Figure 2. The mass fraction gradients  $m_1$  and  $m_2$  are directly related to the separation of the two components nC<sub>12</sub> and THN, respectively, by  $S_1 = m_1 \times A$  and  $S_2 = m_2 \times A$ .

In order to increase the separation level of the mixture, we assess the mass fraction vertical gradient according to a control

TABLE I. Comparison of  $m_k$  values between the different mixture cases,  $Cr_{kj}=0$  and  $Cr_{kj} \neq 0$  ( $j \neq k$ ), according to the temperature gap between the vertical walls.

$\Delta T$ (°C)	$m_1^d$ (m <sup>-1</sup> )		$m_2^d$ (m <sup>-1</sup> )	
	$Cr_{kj}=0$	$Cr_{kj} \neq 0$	$Cr_{kj}=0$	$Cr_{kj} \neq 0$
1	0.1753	0.1806	-0.0895	-0.1936
2	0.3302	0.3360	-0.2268	-0.3614
3	0.4125	0.4196	-0.3343	-0.4525
4	0.4587	0.4660	-0.4085	-0.5035
5	0.4865	0.4934	-0.4587	-0.5338
10	0.5352	0.5394	-0.5570	-0.5849
15	0.5465	0.5495	-0.5817	-0.5962
20	0.5507	0.5532	-0.5911	-0.6003
25	0.5527	0.5550	-0.5956	-0.6023
30	0.5537	0.5559	-0.5981	-0.6034

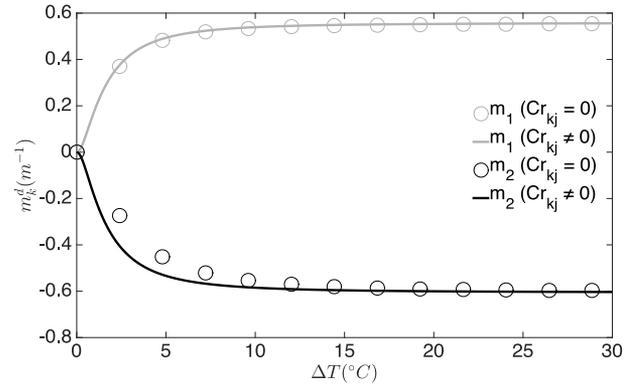


FIG. 2. Variation of the mass fraction gradient of the two components nC<sub>12</sub> (1) and THN (2) for  $Le_1=516.9$ ,  $Le_2=304.2$ ,  $\psi_1=0.256$ ,  $\psi_2=0.144$  in the two cases:  $Cr_{12}=0, Cr_{21}=0$ , and  $Cr_{12}=-0.013, Cr_{21}=-0.704$  (real blend).

parameter such as the cell thickness and the temperature difference between the two vertical walls. Observation of Figure 3 reveals that the separation of the components 1 and 2 is enhanced when the cell's thickness is reduced and the temperature difference is greater.

## B. Assuming the forgotten effect hypothesis

In 1939, Furry, Jones, and Onsager<sup>22</sup> (FJO) established the equations of the balance sheet to describe the thermal gravitational diffusion process for a binary mixture of gas confined in a differential heated, vertical rectangular cavity. However, in this work, they ignored the role of the mass

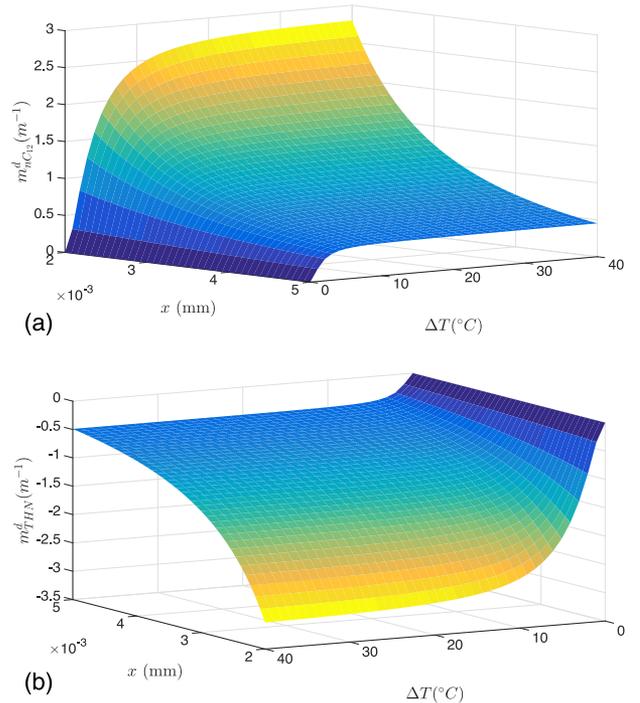


FIG. 3. Dependence of the mass fraction gradient on the temperature difference  $\Delta T$  and the cell thickness for (a)  $n$ -dodecane ( $m_{nC_{12}}^d(x, \Delta T)$ ) and (b) tetralin ( $m_{THN}^d(x, \Delta T)$ ) for  $Le_1=516.9$ ,  $Le_2=304.2$ ,  $\psi_1=0.256$ ,  $\psi_2=0.144$ ,  $Cr_{12}=-0.013$ ,  $Cr_{21}=-0.704$ .

fraction in the body force term because the temperature field settled in the enclosure faster than the mass fraction field did. This hypothesis is often called “the forgotten effect.” The Darcy-Boussinesq equation then becomes

$$\frac{dv}{dx} = Ra \frac{dT}{dx}. \quad (16)$$

By replacing this momentum equation in Eqs. (8), we determine the mathematical expression for the vertical velocity evolution, the mass fraction and the mass fraction gradient of each of the mixture constituents. The

solutions are given by the following Eqs. (17) according to Lewis number, Rayleigh number, and cross-diffusion coefficients.

In order to evaluate the usefulness of the forgotten effect hypothesis, we compared  $m_k^d$  plotted using this hypothesis, and  $m_k^d$  in the general case. Figure 4 shows that, for  $\Delta T \leq 15^\circ\text{C}$ , the forgotten effect hypothesis is not appropriate but, for a temperature difference of more than  $15^\circ\text{C}$ , it provides calculations of good accuracy. In these conditions, we can use this hypothesis and thus greatly simplify the analytical calculations,

$$v(x) = \frac{1}{2} Ra (1 - 2x), \quad (17a)$$

$$C_k(x, y) = m_k y + \gamma_k Ra \left( -\frac{x^3}{6} + \frac{x^2}{4} - \frac{1}{24} \right) - \xi_k x + \frac{1}{2} (\xi_k - m_k A), \quad \forall k = 1, 2, \quad (17b)$$

$$m_k = \frac{10 Ra [Le_k (Le_j Ra)^2 - 120 (Cr_{kj} ((1 - Cr_{jk}) Le_j + Le_k) - Le_k)]}{(Le_k Le_j Ra^2)^2 + 120 [Ra^2 (2 Cr_{kj} Cr_{jk} Le_k Le_j + Le_k^2 + Le_j^2) + 120 (1 - Cr_{kj} Cr_{jk})^2]}. \quad (17c)$$

For  $Cr_{kj} = 0$ , the mass fraction gradient according to the Rayleigh number and the Lewis number of each component are evaluated as follows:

$$m_k = \frac{10 Le_k Ra}{(Le_k Ra)^2 + 120}, \quad \forall k = 1, 2. \quad (18)$$

Solving the problem by excluding the cross-diagonal elements of the diffusion matrix simplifies the analytical calculations hugely, and this is interesting because we have seen that, for a high value of  $\Delta T$  (i.e.,  $\Delta T > 15^\circ\text{C}$ ), there is practically no difference in the results for the two mixture cases (Figure 2). Hence we can give a more general form of the simplified mass fraction gradient of each component of the ternary mixture, see Equation (18).

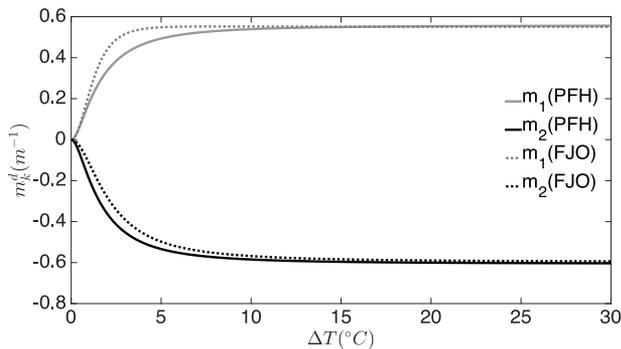


FIG. 4. Variation of the horizontal mass fraction gradient of the two components nC<sub>12</sub> (1) and THN (2) through the temperature difference  $\Delta T$  for  $Le_1 = 516.9$ ,  $Le_2 = 304.2$ ,  $\psi_1 = 0.256$ ,  $\psi_2 = 0.144$ ,  $Cr_{12} = -0.013$ , and  $Cr_{21} = -0.704$ .

#### IV. NUMERICAL SIMULATION

The system of Eqs. (3) with the boundary conditions (4) presented above was solved numerically by a finite element method (Comsol Multiphysics industrial code). This modeled problem uses structured meshes that are better suited to the rectangular shape of the cell. The aspect ratio of the cell studied was 15. The spatial resolution for this aspect ratio is  $20 \times 150$  for low  $\Delta T$  (i.e.,  $1 \leq \Delta T (^\circ\text{C}) \leq 4$ ) but should be  $20 \times 300$  for larger temperature differences to increase the accuracy. The aim of this numerical simulation was to assess the influence of the temperature difference  $\Delta T$  (single control parameter) on the vertical mass fraction gradient (i.e., the separation level). Table II compares the values of  $m_k$  determined by numerical simulation with the theoretical values calculated by the two different analytical methods.

The variation of the mass fraction gradient of *n*-dodecane (nC<sub>12</sub>) and tetralin (THN) according to the temperature

TABLE II. Comparison of the  $m_k$  for the three methods presented previously.

$\Delta T (^\circ\text{C})$	$m_1^d (m^{-1})$			$m_2^d (m^{-1})$		
	PFH	FJO	Numeric	PFH	FJO	Numeric
1	0.181	0.226	0.181	-0.194	-0.117	-0.195
2	0.336	0.440	0.336	-0.361	-0.281	-0.365
3	0.420	0.516	0.420	-0.453	-0.391	-0.459
4	0.466	0.540	0.466	-0.504	-0.457	-0.508
5	0.493	0.548	0.494	-0.534	-0.498	-0.535
10	0.539	0.552	0.539	-0.585	-0.568	-0.586
15	0.550	0.551	0.550	-0.596	-0.584	-0.598
20	0.553	0.551	0.553	-0.600	-0.590	-0.602

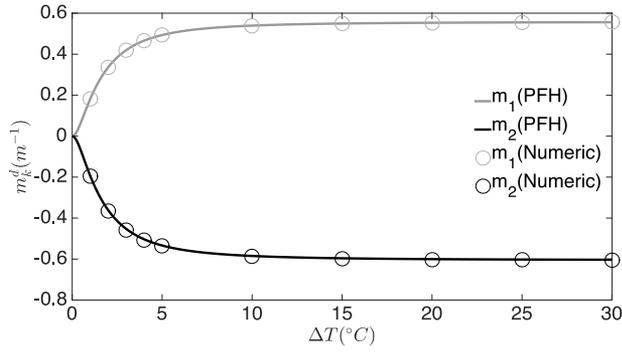


FIG. 5. Dependence of the horizontal  $nC_{12}$  (1) and THN (2) mass fraction gradients according to the temperature difference  $\Delta T$  for  $Le_1 = 516.9$ ,  $Le_2 = 304.2$ ,  $\psi_1 = 0.256$ ,  $\psi_2 = 0.144$ ,  $Cr_{12} = -0.013$ , and  $Cr_{21} = -0.704$ .

difference  $\Delta T$  is plotted in Figure 5. Good similarity between the theoretical results and the numerical simulation can be observed whatever the Rayleigh number. This validates the hypothesis of parallel flow and also confirms the Furry, Jones, and Onsager hypothesis of neglecting the effect of the mass fraction in the convection term generator in the momentum equation. Figure 6 gives a qualitative representation of mass fraction fields for  $n$ -dodecane 6(a) and tetralin 6(b). The simulation was performed for optimal Rayleigh number ( $Ra_{opt} = 0.017$ ) and it can be observed that tetralin separated more than  $n$ -dodecane, due to cross-diffusion effects.  $Cr_{21}$  was much higher than  $Cr_{12}$ . The convective flow was multicellular and it was not possible to achieve the separation of the components. Figure 7 shows a representation of the isotherms 7(a) and streamlines 7(b). The monocellular nature of the convective flow is clearly visible. This type of flow favors the separation of a complex mixture.

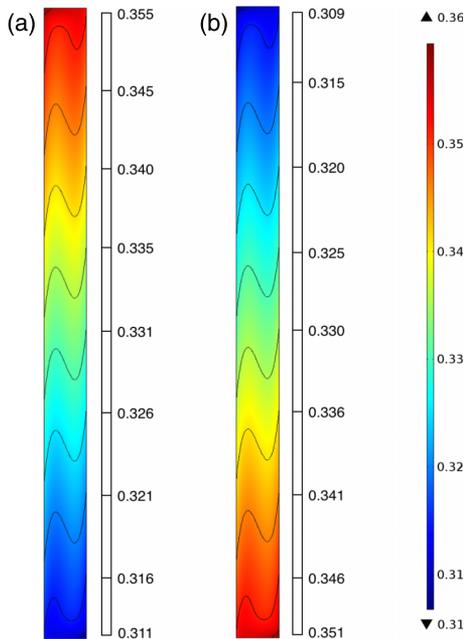


FIG. 6. Evolution of the mass fraction of components  $n$ -dodecane ( $C_{nC_{12}}^d(x, y)$ ) (a) and tetralin ( $C_{THN}^d(x, y)$ ) (b),  $\varepsilon = 0.25$ ,  $A = 15$ ,  $\Delta T = 15^\circ C$  and all other parameters are kept constants.

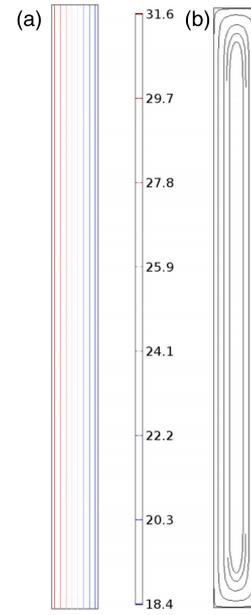


FIG. 7. Isotherms (a) and streamlines (b) evolution in the enclosure;  $\varepsilon = 0.25$ ,  $A = 15$ ,  $\Delta T = 15^\circ C$  and all other parameters are kept constants.

## V. EXPERIMENTAL COMPARISON

Work by Costesèque and Loubet,<sup>23</sup> which was mainly experimental, showed the variation of mass fractions for the constituents of a ternary mixture of hydrocarbons undergoing thermal gravitational diffusion in porous packed columns. The hydrocarbons chosen:  $n$ -dodecane ( $nC_{12}$ ), isobutylbenzene (IBB), and tetralin (THN) were a mixture of qualitatively modeled oils of an oil-field in the North Sea. The mass fraction of each component was measured according to the height in the porous column under identical thermal and dimensional conditions and after the time necessary to obtain a quasi-steady state (approximately 50 days). To show possible segregations in natural oils, there were five regularly spaced sampling ports in the walls for measuring the mass fractions at different levels:  $H = 0$  (bottom),  $H = L/4$ ,  $H = L/2$ ,  $H = 3L/4$ , and  $H = L$  (top). For each sample (with a volume of a few micro-liters) the relative mass fraction of each component was measured by gas chromatography. The chromatograph used is DI 200 type with a semi-polar column G. Williams Scientifics.

The column was 60 cm high and 0.45 cm thick. The average temperature was  $43.5^\circ C$  and the difference in real temperature between the two walls (hot and cold) was  $14^\circ C$ . The porous lining saturated with ternary solution consisted of pseudospherical zirconium oxide ( $ZrO_2$ ) grains. Hence, the cell porosity was about 0.4. This affected the diffusion time of the mixture, and therefore the time to reach the steady state. The intrinsic permeability of the porous medium was  $1.1 \times 10^{-10} m^2$  and the experimental Rayleigh number was thus estimated at 0.19. To validate our whole study (analytical solution and numerical simulation), the results are compared with experimentally measured values in Figure 8. There is very good agreement among the solutions obtained numerically, analytically following the two approaches by the parallel flow approximation and the FJO hypothesis, and experimentally.

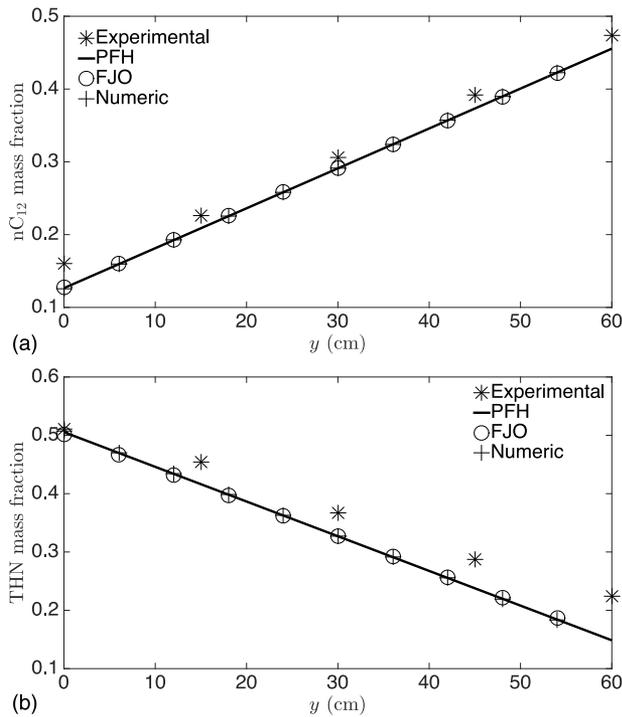


FIG. 8. Evolution of the mass fraction of the two components  $C_{nC_{12}}^d(y)$  (a) and  $C_{THN}^d(y)$  (b) along the thermal gravitational column for  $Le_1 = 516.9$ ,  $Le_2 = 304.2$ ,  $\psi_1 = 0.256$ ,  $\psi_2 = 0.144$ ,  $Cr_{12} = -0.013$ , and  $Cr_{21} = -0.704$ .

## VI. CONCLUSION

This study makes a contribution to the problem of separation of ternary mixture components by thermal gravitational diffusion. The problem of thermosolutal convection in a vertical porous cavity saturated by the DCMIX1 ternary mixture was studied. The thermal and geometrical configurations chosen led to the existence of a mono-cellular flow. This type of flow is ideal, as it promotes the separation of a complex fluid species. A theoretical solution was presented following two different approaches and a numerical simulation was performed to determine the evolution of the velocity, the temperature, and the mass fractions within the cavity in the steady state. To complete this study, the analytical and numerical results were compared with experimental results (Costesèque *et al.*<sup>23</sup>). Across a comparative study, the different results showed very good agreement, which led to endorse the outlined assumptions. Moreover, the mixture separation in the case of a ternary with mass cross-diffusion equals zero and for real fluids was compared analytically according to the

temperature difference. In both cases, the maximum separation was the same. Ultimately, the work very strongly supports the experimentally determined transport coefficients published recently in *J. Chem. Phys.*<sup>9,21</sup> In the light of all the problems encountered with the measurement of transport coefficients of ternary mixtures, this confirmation of experimental results by a completely different technique is an essential outcome with importance for other researchers.

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