Separation of a binary liquid mixture in compound system: Fluid–porous–fluid

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**Abstract**

We report results on a computational study of double-diffusive convection with Soret effect in a system consisted of a fluid region adjacent to a porous medium, which is saturated with the same liquid. The liquid is a binary mixture with positive Soret coefficient. The flow in the system is driven by buoyancy force due to imposed temperature difference between lateral walls. The study is focused on components separation due to the Soret effect through the porous medium in presence of liquid regions near its side walls. The problem is solved in each domain independently. A non-stationary Darcy–Brinkman model is used to calculate momentum, heat and mass transport and continuity equations in the porous medium, while full Navier–Stokes equations are solved in the pure fluid. It is demonstrated that presence of free liquid volumes near the lateral walls strongly affect the process of separation in the porous medium.

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1. Introduction

Interest to double-diffusive convection in porous media has been motivated by diverse engineering problems. The related problems of composite systems, consisting of liquid layers adjacent to porous bodies has received significant attention due to environmental (ground-water flow, CO\textsubscript{2} leakage through abandoned wells) and industrial (solid matrix heat exchangers, post-accident cooling of nuclear reactors) applications, especially in petroleum industry.

Thermodiffusion (or Soret effect) is a subtle second-order molecular transport of substances associated with a thermal gradient. In response to an imposed thermal gradient \( VT \), concentration gradients \( VC \) appear in originally uniform mixture. The separation is counteracted by the molecular diffusion, which aims at eliminating the concentration variations. The total mass flux of a component with a spatial distribution of concentration \( C \) through a surface is a sum of convective, diffusive and thermodiffusive currents:

\[
J_C = \rho_0 \left( \bar{V} C - D V C - D T C_0 (1 - C_0) \nabla T \right),
\]

where \( S_T = DT/D \) is the Soret coefficient, \( D \) and \( DT \) are the diffusion and thermodiffusion coefficients, \( \bar{V} \) is velocity of the medium, \( C \) and \( T \) are mass concentration and temperature. \( C_0 \) is the mass fraction of the denser component in the solution.

A steady state is reached when the separating effect of thermodiffusion is balanced by the isothermal diffusion in opposite direction. In a motionless medium at the steady state the mass flux is equal to zero

\[
J_C^0 = - \rho_0 [D V C + D T C_0 (1 - C_0) \nabla T] = 0.
\]

Correspondingly, the separation achieved at the steady state will be

\[
\Delta C = - S_T C_0 (1 - C_0) \Delta T,
\]

where \( \Delta T = T_{\text{hot}} - T_{\text{cold}} \) is the imposed temperature difference.
Sign of the Soret coefficient is the indicator of the direction of the separation of the components. In binary mixtures, one can distinguish positive Soret effect \( (S_T > 0) \) when denser component migrates toward the cold side, and negative Soret effect \( (S_T < 0) \) when the direction of the migration is the opposite. A linear static concentration profile is established in the direction of the temperature gradient. It follows naturally from Eq. (3) that the Soret coefficient may be experimentally determined via performing measurements of the magnitude of the relative separation \( \Delta C \) in the mixture in a cell at its cold and hot ends.

Any motion provokes mixing of species and decreases the separation in the direction of the imposed \( \nabla T \). Shevtsova et al. [1] investigated the effect of the convection due to static acceleration \( g \) perpendicular to the imposed \( \nabla T \) in a wide range of \( 0 < g/g_0 < 0.01 \), here \( g_0=9.81 \text{ m/s}^2 \) is the earth gravity. Besides proving that increasing the gravity decreases the components separation via intensifying the flow, it was also found that the stronger the convective mixing is, the faster the concentration field attains its steady state.

While Clusius–Dickel thermogravitational columns [2] make use of the natural convection to enhance the separation in the direction perpendicular to \( \nabla T \) as well as to measure the Soret coefficient, fluid flows are undesirable in many other configurations. For instance, an experimental configuration allowing a fluid motion to occur is irrelevant for an accurate measurement of \( S_T \) in "convection-free" static cells [3]. To avoid the perturbing effect of gravity, measurements of the Soret coefficient might be performed in microgravity environment, but at very high experimental costs. On Earth, while positive Soret coefficient might be measured in a pure fluid in static cells by imposing a vertical temperature gradient, a convective instability will be induced if the Soret effect is negative [4–6], resulting from accumulation of the denser component over the less denser one. Nevertheless, the negative Soret coefficients can be deduced from the value of the critical temperature difference, at which the instability starts. But obtained thereby results are usually not reliable due to insufficient accuracy of the experimental techniques [7].

Recently, attempts were undertaken for measuring the Soret coefficients in laboratory experiments by using packed thermal diffusion column device (PTC) [8,9], which is a compound system porous media-free fluid (see Fig. 1). Porous medium is a material consisting of a solid matrix with interconnected voids (pores) containing the fluid. Convection is damped there due to small size of the pores. In turn, the transparent free fluid zones allow applying different optical methods for measuring the separation \( \Delta C \) there. However, the measured thermodifusion coefficients were consistently larger than the corresponding values known from the literature. One of reasons of this discrepancy could be the presence of the porous-free fluid interfaces in those setups. When two media with essentially different both transport properties and different transport characteristic times (thermal and solute) are in contact, the local thermal and solute gradients at the contact surface get modified. It results in a modification of the global fluxes through the system. This phenomenon of the modification of the transport was disregarded in [8], but it should play an important role both on ground and in microgravity.

The present study analyzes the Soret separation by thermodiffusion of components of a binary liquid mixture through a porous medium. To clarify the mechanism by which the convective flow in the adjacent liquid may affect this separation, modeling was performed separately in the pure fluid and in porous medium. We choose this approach, rather than solving the problem in the whole domain, because it is more conducive to explaining qualitatively the processes occurring at the permeable fluid–porous interface. To analyze the components separation in presence of different phenomena (e.g. convection in multicomponent liquid), we calculate a parameter called Soret separation
\[
S_R = |C_{\text{hot}} - C_{\text{cold}}|/\Delta C,
\]
which is the absolute value of the difference between mean concentrations at the cold and hot walls, scaled by \( \Delta C \) defined by Eq. (3). At steady state in a motionless medium \( S_R \) attains its maximum value, i.e. \( S_R = 1 \). Since a motion of the fluid tends to reduce the separation [1], then \( S_R < 1 \).

2. Model

The considered system consists of two free fluid domains coupled with a saturated porous medium (Fig. 1). We will also refer to them as fluid and porous zones respectively. There exist different approaches to describe flow in multi-domain system. The most used approach consists of the Navier–Stokes equations in the pure liquid and the Darcy equation in the porous medium, with further need to find relevant boundary conditions at the interface between them (see e.g. [10]).

In the present study, the problems in both domains were solved separately. However, taking convection into account, the non-stationary Darcy–Brinkman model is used in the porous domain [11]. The following dimensional nonlinear time-dependent momentum, continuity, energy, and mass conservation equations governing the evolution of the system are solved:
\[
\frac{1}{\phi} \frac{\partial \mathbf{V}_{\text{por}}}{\partial t} + \frac{1}{\phi^*} (\mathbf{V}_{\text{por}} \cdot \nabla) \mathbf{V}_{\text{por}} = -\frac{1}{\mu_0} \nabla P + v_e \nabla^2 \mathbf{V}_{\text{por}} + \rho \Phi (1 - \beta (T - T_0)) + \beta C (C_{\text{por}} - C_0) + \frac{v_{\text{lip}}}{K} \mathbf{V}_{\text{por}},
\]

Fig. 1. Geometry of the problem. Fluid and porous zones heated at opposite walls.
\[ \nabla \cdot \mathbf{V}_{\text{por}} = 0, \]  
\[ (\rho C_p)_{\text{por}} \frac{\partial T}{\partial t} + (\rho_0 C_p)_{\text{liq}} (\nabla \mathbf{V}_{\text{por}} \cdot \nabla) T = k_{\text{por}} \nabla^2 T, \]  
\[ \phi \frac{\partial C}{\partial t} + (\nabla \mathbf{V}_{\text{por}} \cdot \nabla) C = \phi D_{\text{por}} (\nabla^2 C + S_T C_0 (1-C_0) \nabla T), \]  
where \( \mathbf{V}, T \) and \( C \) are velocity, mass fraction and temperature respectively. \( \phi \) is the porosity, \( C_p \) is the heat capacity and \( D \) is the diffusion coefficient.

We work with dimensionless governing equations (not given). Taking the size of the cell in the direction of the imposed temperature gradient \( L \) as the length scale, one can now introduce the velocity, time, pressure, temperature and concentration scales as

\[ [V] = v_{\text{liq}} / L, \quad [t] = L^2 / v_{\text{liq}}, \quad [P] = \rho_0 v_{\text{liq}}^2 / L^2, \quad [T] = \Delta T, \quad [C] = \Delta C. \]

Dividing each variable by its scale the governing equations (5)–(12) can be normalized. The dimensionless concentration is introduced as \( c = (C-C_0)/\Delta C \).

The goal of the calculations is to model an experiment [9] and to understand physical phenomena taking place in the system. We do not perform quantitative comparison as the experimental results are not yet published. However, the choice of working materials, size of the domain and value of \( \Delta T \) are corresponding to the experimental setup. In the experiment, the porous zone is bounded from both sides by two identical liquid volumes (see the sketch on Fig. 1), and thus there are two liquid–porous interfaces. We shall model only one liquid volume as the flow in the second one is the same because of the geometrical symmetry of the problem. The liquid is 50\% 1,2,3,4-tetrahydronaphthalene (THN)-dodecane solution with properties given in Table 1.

The fluid zone is 10 mm high and 6 mm long, and the porous zone is 10 mm high and 33 mm long, yielding the size of the cell \( L=45 \) mm, with the properties given in

### Table 1

<table>
<thead>
<tr>
<th>Property</th>
<th>THN-C_{13}H_{26}</th>
<th>Porous medium in silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density ( \rho ) (kg/m(^3))</td>
<td>841</td>
<td>1530</td>
</tr>
<tr>
<td>Kinematic viscosity ( v ) (m/s)</td>
<td>( 1.46 \times 10^{-6} )</td>
<td></td>
</tr>
<tr>
<td>Heat capacity ( C_p ) (J/(kg K))</td>
<td>2000</td>
<td>1090</td>
</tr>
<tr>
<td>Thermal conductivity ( k ) (W/m K)</td>
<td>0.13</td>
<td>0.755</td>
</tr>
<tr>
<td>Thermal diffusivity ( a ) (m(^2)/s)</td>
<td>( 7.73 \times 10^{-8} )</td>
<td>( 4.53 \times 10^{-7} )</td>
</tr>
<tr>
<td>Thermal expansion ( \beta_t ) (1/K)</td>
<td>( 8.96 \times 10^{-4} )</td>
<td></td>
</tr>
<tr>
<td>Solutal expansion ( \beta_c )</td>
<td>0.236</td>
<td></td>
</tr>
<tr>
<td>Diffusion coefficient ( D ) (m(^2)/s)</td>
<td>( 6.21 \times 10^{-10} )</td>
<td></td>
</tr>
<tr>
<td>Soret coefficient ( S_T ) (1/K)</td>
<td>( 9.5 \times 10^{-3} )</td>
<td></td>
</tr>
<tr>
<td>Porosity ( \phi )</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>Permeability ( K ) (m(^2))</td>
<td>1.97 \times 10^{-12} = \text{2 Darcy}</td>
<td></td>
</tr>
<tr>
<td>Tortuosity ( \tau )</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
Table 1. Initially the mixture is homogeneous and due to the positive Soret effect the less dense liquid is accumulated near the hot wall. The imposed temperature differences on the fluid and the porous zones in the horizontal direction are $\Delta T_{\text{liq}} = 0.67 \text{ K}$ and $\Delta T_{\text{por}} = 3.67 \text{ K}$, and thus the imposed temperature gradients in both zones are the same.

The characteristic time to achieve the thermal conductive stationary state is $\tau_{\text{th}} = L^2/(\pi^2 a)$, where $L$ is the size of the medium along the imposed thermal gradient, and $a$ is the thermal diffusivity defined by $a = k/(\rho C_p)$. Because the thermal time is at least 125 times smaller than the diffusion time $\tau_D = L^2/(\pi^2 D)$, a linear temperature profile is rapidly established in the porous medium while the concentration variation is not yet noticeable.

The following boundary conditions are used: zero velocity $\dot{V} = 0$ at the rigid walls. At the liquid–porous interface, zero velocity component ($\dot{V} = 0$) is assumed to be valid at the first step. Thermal conditions are constant temperatures at the two opposite side walls $T(x = 0) = T_{\text{hot}}$, $T(x = 1) = T_{\text{cold}}$; the horizontal walls are thermally insulated with adiabatic boundary conditions: $(\partial T/\partial h)(z = 0,1) = 0$. Absence of the mass flux at the impermeable rigid walls gives: $(\partial C/\partial h) + S_f C_0(1-C)\partial T/\partial h = 0$.

3. Results and discussion

Initially the liquid is motionless with uniformly distributed temperature $T_{\text{cold}}$ and concentration $C_0$. The very small permeability of the solid matrix creates a very high resistance to the liquid flow. Consequently, the Soret separation $S_R$ is almost equal to unity (Table 2). The comparison is made for the values at the steady state. In both zones the flow pattern is one vortex occupying the whole domain, in the porous medium the vortex is symmetrical (Fig. 2(b)) while in the liquid it is slightly distorted along the diagonal (Fig. 2(a)). It is a clear sign of the stronger convection in this zone. In the fluid volume the convective flow is more than 800 times stronger; the Nusselt number reaches a value of 2.5 indicating that the convective heat transport is much stronger than the conductive one characterized by $Nu = 1$. The convection mixes the fluid and it results in a small value of the Soret separation, which is only $S_R = 0.161$ (Table 2).

The mass transport in the porous zone is very slow and the diffusion transport dominates over the convective one. The strength of the convection grows with increasing of the temperature difference, but still is weak for $\Delta T$ of interest. The maximum velocity of the liquid in the porous medium and estimations of the fluid particle displacement due to the convection during 10 h of observations are given in Table 3 for $\Delta T_{\text{por}} = 1.3$ and 5 K. Note, that the displacement of the fluid particle by diffusion during 10 h is about $\Delta x_D = 1.5 \text{ mm}$ while by convection is only $\Delta x_{\text{conv}} = 0.324 \text{ mm}$ at $\Delta T = 5 \text{ K}$. So, primarily idea about using porous medium as a convection free environment for measuring the diffusion and Soret coefficients looks attractive. However its realization imposes limitations as any additional liquid motion changes both the heat and mass transport.

The effect of the permeability $K$ alone on the strength of the convection in the porous medium is considerable. Being strongly controlled by pore size, permeability characterizes frictional resistance of the porous medium to flow. Body with small pores (small $K$) has a high ratio of surface area to pore volume, and thus high resistance. Fig. 3(a) demonstrates this as the maximum value of the velocity of the natural convection $V_{\text{max}}$ in the domain versus $K$. $V_{\text{max}}$ grows linearly with increasing the permeability, with a slope of $3 \times 10^{-9} \text{ m/s (Darcy)}$. As the convective circulation in the porous zone strengthens with the increase of $K$, mixing becomes strong and expectedly $S_R$ decreases (Fig. 3(b)). Even though the flow in the porous zone is weak even at $K = 1000 \text{ Darcy}$, the decrease of the separation is remarkable. The rate of the mixing is very high in the range $0 < K < 100$. At $K = 100 \text{ Darcy}$, $S_R$ is approximately 3 times smaller than at $K = 2 \text{ Darcy}$.

The established concentration profiles $C$ along the horizontal (between the hot and cold walls) and vertical central lines in both zones are shown on Fig. 4. While $C(x)$ is expectedly linear in the porous zone (Fig. 4(b)), in the pure liquid it consists of a vast central part of a uniformly mixed liquid and two boundary layers near the opposite walls (Fig. 4(a)). Thus the separated components get accumulated in the thin regions near the hot and cold walls, where the flow is relatively weak. The concentration profile has a similar shape along the central vertical line in the fluid zone (Fig. 4(c)). The two boundary layers at the top and bottom are a product of the convective roll spreading the components from the boundary layers along the walls and making the fluid zone to be similar to a vertical thermogravitational column [13]. At the same

![Fig. 2. Pattern flow in steady state due to side heating are shown as stream function in pure liquid (a) and in the porous zone (b).](image-url)
time, no significant separation in the vertical direction is observed in the porous zone; it is only about 1.5% of the separation between the opposite hot and cold boundaries.

The dynamics of the components separation is shown on Fig. 5. Since the characteristic time $\tau_D$ to achieve the pure thermodiffusion stationary state in the porous zone is very large, it does not come as a surprise that it takes almost 200–300 h for the separation to attain the steady state (Fig. 5(b)). The fluid zone is 5.5 times shorter, and $\tau_D$ would be almost 30 times less there. $S_R$ achieves its steady state even faster (see also Table 2) because of the strong convective flow in the fluid zone [1]. It occurs within approximately 1–2 h (Fig. 5(a)).

Having analyzed the dynamics of the separation in both media, let us now turn to the question of what would happen in the system if the fluid and the porous zones have a permeable interface between them. The two media have different transport properties, resulting in a discontinuity of the gradients of the transported variables at the interface, while both temperature and mass fraction are continuous functions. Assuming velocity normal to the interface is zero (only pure diffusive transport takes place there [14]), and in absence of any local thermal energy and mass sources at the interface, one may write down the following conservation laws:

$$\left(\frac{\partial T}{\partial \mathbf{n}}\right)_{\text{por}} = \frac{k_{\text{liq}}}{k_{\text{por}}} \left(\frac{\partial T}{\partial \mathbf{n}}\right)_{\text{liq}},$$  \hspace{1cm} (14)

$$\left(\frac{\partial C}{\partial \mathbf{n}}\right)_{\text{por}} = \frac{\tau^2}{\phi} \left(\frac{\partial C}{\partial \mathbf{n}}\right)_{\text{liq}} + S_R C_0 (1-C_0) \left(\frac{\tau^2}{\phi} \frac{k_{\text{liq}}}{k_{\text{por}}} \left(\frac{\partial T}{\partial \mathbf{n}}\right)_{\text{liq}}\right),$$  \hspace{1cm} (15)

where $\mathbf{n}$ is a unity vector normal to the interface.

Both different times of achieving the pure thermodiffusion steady state and the generation of the boundary
layers are very important features for the mass transfer in the transients when the two zones are in contact. Since the concentration is a continuous function and the separation in the fluid zone is faster at the beginning at the process, this should inevitably lead to a growth of the concentration at the interface in the porous zone. In turn, the solute gradient in the porous zone should adjust itself to $\nabla C$ in the liquid at the interface so that the interfacial conditions equations (14) and (15) are met, i.e.

$$
\left( \frac{\partial T}{\partial n} \right)_{\text{por}} = 0.17 \left( \frac{\partial T}{\partial n} \right)_{\text{liq}},
$$

$$
\left( \frac{\partial C}{\partial n} \right)_{\text{por}} = 2.2 \left( \frac{\partial C}{\partial n} \right)_{\text{liq}} + 2.05 S_T C_0 (1 - C_0) \left( \frac{\partial T}{\partial n} \right)_{\text{liq}}
$$

for the parameters tabulated in Table 1. As it was shown, $\nabla C_{\text{liq}}$ in the liquid at the interface is large (Fig. 4(a)), and so $\nabla C_{\text{por}}$ will inevitably be also large. To maintain the high gradient of the concentration, more solvent is necessary. It will be supplied by the interface, which gets the solvent from the fluid, resulting in generating an intensive diffusive mass flux into the porous region. It turns out that the fluid zone plays a role of a donor while at the opposite side (in the second fluid zone) the porous medium is the donor. Due to the very slow nature of the diffusive process this additional mass flux will gradually be enriching the porous media near the hot side and impoverishing it at the cold side. Correspondingly, the concentration in the pure liquid will decrease at the hot side and increase at the cold side. This “interfacial pumping” is a feature of the transients, and the longer the time required for reaching the steady state, the more solute will be pumped out of (or into) the corresponding fluid volume.

The process described above considerably accelerates the mass transport through the porous media in transients regime. On the other hand, the volume mean concentration in the fluid zone, which feeds the porous medium at the hot side, is decreasing. By analogy, the mean concentration in the pure liquid at the cold side is increasing. This is why attempts of measuring the Soret coefficient by observing transients of the separation in the fluid volumes will yield a higher value of $S_T$.

To follow the dynamics of the Soret separation more precisely, the problem should be solved in the entire system, and it is one of the goals of future study.

### 4. Conclusions

We have analyzed the separation by Soret effect of components in a binary mixture in fluid and in porous domains in presence of gravity field. In particular, we have focused our attention on a question of how heat and mass transfer in the fluid zone affects dynamics of the separation in the adjacent porous medium.

As a result of the buoyant convection, the concentration field in pure liquid is uniform in the central part, creating pronounced boundary layers at the border. Convection in porous media is at least thousand times weaker and the mass transport is controlled by diffusion. The boundary layer with a large gradient of concentration in the liquid adjacent to the porous region generates a strong mass flux from the fluid to the porous medium at the hot side and in the opposite direction at the cold side. This accelerates the mass transport in the system, which in course of time leads to a strong effect on the components separation.

Based on the findings, one may conclude the following. Measuring the concentration difference in transient regime between the two fluid zones, bounding the porous medium at the opposite sides, with a purpose to calculate the Soret and diffusion coefficients, one will obtain higher than the real values of the coefficients.

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### References


