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Behaviour of a Ternary Mixture with the Net Separation Ratio Close to Zero

Tatyana Lyubimova[1,2], Sergei Prokopev[1,a] and Valentina Shevtsova[3,4]

[1]Institute of Continuous Media Mechanics UB RAS, Perm, Russia
[2]Perm State University, Perm, Russia
[3]Mechanical and Manufacturing Department, Mondragon University, Loramendi 4, Apdo.23, 20500 Mondragon, Spain
[4]Basque Foundation for Science, Bilbao, Spain

E-mail: [a] prokopev.s@icmm.ru

Abstract. The behaviour of the ternary hydrocarbon mixture of toluene-methanol-cyclohexane in mass proportion 0.62/0.31/0.07 is studied. The direct numerical simulation is carried out for the two-dimensional closed cavity heated from above. The mixture is supposed to be in the gravity field. The behavior of the mixture is predominantly caused by the Soret effect (thermal diffusion). An important parameter, responsible for the Soret effect, is the net separation ratio, Ψ. For the mixture under consideration, the two sets of values of Ψ are known. In both cases, the values of Ψ turn out to be close to zero, but in one case Ψ is slightly positive, and it is slightly negative in the second one. This results in qualitative difference in the evolution of the mixture under consideration. If $\Psi > 0$, the mixture comes to the mechanical equilibrium. If $\Psi < 0$, we observe the system to be at the border of stability, under small perturbation there is no instability, but for the perturbation amplitude higher than a threshold value of the convective single-vortex flow arises.

1. Introduction

In a pure single component fluid we normally take into account the effects of convection and thermal conductivity. In binary systems diffusion and thermal diffusion (the Soret effect or also Thermophoresis) come into play. In multicomponent mixtures with three or more components the effects mentioned above are also presented but considerably sophisticated by interactions of components, cross-diffusion, different typical diffusivity times and others. Thermal diffusion takes a special place here. Although the magnitude of component separation usually does not exceed a couple of percent, this phenomenon can make the difference concerning the issue of convection stability. For example, such mixtures are possible, whose components have opposite signs of the Soret coefficients and, accordingly, opposite directions of the thermal diffusion flow. Multicomponent homogeneous mixtures matter in the various fields of natural and industrial interest. Thermal diffusion can enhance the isotope separation that is helpful in the enrichment of Uranium and other elements [1], particularly but not exclusively it could be also important in the radioactive waste storage [2][3]. The Soret effect plays a significant role in such fields as the growing silicon crystals [4], solar ponds (thermal energy collectors) [5][6], biological fluids [7] and others.

In some cases, it could be difficult to measure parameters of mixtures, whether physical experiments [8] or modelling (e.g., the molecular dynamics methods [9][10]) and values of the parameters may have some uncertainties. However, as a rule, the behaviour of liquids is qualitatively identical within the measurement error. In the current paper, we consider the ternary hydrocarbon liquid toluene-methanol-cyclohexane with the mass fraction 0.62/0.31/0.07, respectively. The physical parameters of the mixture are quite typical for liquids (Table 1). The Soret coefficients are obtained from the DCMIX projects as a result of processing the experimental data [8]. Two different

methodologies of the two independent groups gave the very close values of the Soret coefficients. In both cases the net separation ratio was close to zero, but one approach gave the slightly positive value, while in the second one Ψ was slightly negative (Table 2).

The aim of the current paper is to numerically model and analyse the behaviour of the ternary mixture toluene (0.62)-methanol (0.31)-cyclohexane (0.07) for the two sets of thermal diffusion parameters, obtain in the work [8] and listed in Table 2.

Table 1. Physical properties of the liquid toluene(0.62)-methanol(0.31)-cyclohexane(0.07) at temperature T_0=298.15 K.

ρ kg/m^3	$\beta_T/10^{-3}$ kg/m^3	β_{C1}	β_{C2}	$\mu/10^{-3}$ $Pa \cdot s$	$\nu/10^{-6}$ m^2/s	$\chi/10^{-7}$ m^2/s
829.99	1.16	-0.140	-0.048	0.56	0.67	0.94

Table 2. Diffusion and thermal diffusion parameters. The diffusion coefficients $D_{ij}/10^{-9}m^2/s$, the Soret coefficients $S_{T,i}/10^{-3}\mathrm{K}^{-1}$ and the separation ratio coefficients ψ_i and their sum Ψ.

D_{11}	D_{12}	D_{21}	D_{22}	$S_{T,1}$	$S_{T,2}$	ψ_1	ψ_2	Ψ
2.244	1.337	-0.226	0.551	0.504	-1.098	0.0608	-0.0454	0.0154
				0.387	-1.145	0.0467	-0.0473	-0.0006

2. Problem formulation

We consider the Soret-driven convection-diffusion process in the enclosed rectangular 2D cavity with rigid impermeable borders. The sketch of the computation domain, which has the aspect ratio equal 3:1, is depicted in Fig.1. We consider the heating from above with the temperature difference between top and bottom walls equal to 6 °C. The liquid under consideration is the mixture toluene-methanol-cyclohexane with mass fractions 0.62/0.31/0.07.
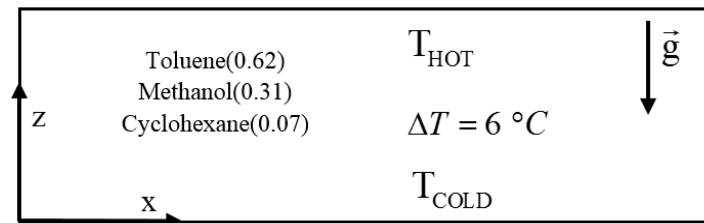
Figure 1. Problem configuration.

It is assumed that the temperature, T, the concentration, $\boldsymbol{C} = (C_1, C_2)$, and the mixture density, ρ, are related by the equation of state

$$\rho = \rho_0\big(1 - \beta_T(T - T_0) - \boldsymbol{I} \cdot B(C - C_0)\big) \tag{1}$$

Here ρ_0, T_0, C_0 denote the reference density, temperature and concentration, β_T is the thermal expansion coefficient, $\boldsymbol{I} = (1,1)$ is the unit vector, $B = \mathrm{diag}(\beta_{C1}, \beta_{C2})$ is the diagonal matrix of the solute expansion coefficients.

The governing equations we use are the Nervier-Stocks equations in the Boussinesq approximation[11], coupled with the heat equation and the Fick equation (Two equations for concentration components are used, the third one is dependent on the others, $C_1 + C_2 + C_3 = 1$). We provide these equation written in the dimensionless form. As scaling factors, we introduce the following dimensionless units, h for the length, h^2/ν for the time, ν/h for the velocity, $\rho_0 h^2/\nu^2$ for the pressure, $\Delta T = T_{hot} - T_{cold}$ for the temperature and $\beta_T \Delta T B^{-1}$ for the concentration.

$$\frac{\partial \vec{V}}{\partial t} + \vec{V} \cdot \nabla \vec{V} = -\nabla p + \Delta \vec{V} + \frac{\mathrm{Ra}}{\mathrm{Pr}}(T + \boldsymbol{I} \cdot \boldsymbol{C})\vec{e} \tag{2}$$

$$\mathrm{div}\, \vec{V} = 0 \tag{3}$$

$$\frac{\partial T}{\partial t} + \vec{V} \cdot \nabla T = \frac{1}{\mathrm{Pr}}\Delta T \tag{4}$$

$$\frac{\partial \boldsymbol{C}}{\partial t} + \vec{V} \cdot \nabla \boldsymbol{C} = SC(\Delta \boldsymbol{C} - \boldsymbol{\psi}\Delta T) \tag{5}$$

The following dimensionless parameters are introduced here, $\mathrm{Ra} = g\beta_T \Delta T h^3/\chi\nu$ is the Rayleigh number, $\mathrm{Pr} = \nu/\chi$ is the Prandtl number, $SC = \nu^{-1}BDB^{-1}$ is the 2×2 matrix of modified Schmidt numbers, $\psi_i = -\beta_{C,i}/\beta_T\,(D)_{ik}^{-1}D_{T,k} = -\beta_{C,i}/\beta_T\,S_{T,i}$ are separation ratios. Their sum, $\sum_i^n \psi_i = \Psi$ is called the net separation ratio. $S_{T,i} = (D)_{ik}^{-1}D_{T,k}$ and $D_{T,k}$ $(i,k = 1,2)$ are the Soret and thermal diffusion coefficients, respectively. $\vec{V} = (v_x, 0, v_z)$ stands for the vector of dimensionless velocity, p is dimensionless pressure. ν and χ are the kinematic viscosity and the thermal diffusivity, g is the amplitude of the gravity acceleration.

Equations (2)-(5) should be completed with the boundary conditions.

$$z = 0,1: \quad \vec{V} = 0, \quad T(z = 0) = 0, \quad T(z = 1) = 1 \tag{6}$$

$$z = 0,1: \quad \frac{\partial \boldsymbol{C}}{\partial z} - \boldsymbol{\psi}\frac{\partial T}{\partial z} = 0 \tag{7}$$

$$x = 0,3: \quad \vec{V} = 0, \quad T = z, \quad \frac{\partial \boldsymbol{C}}{\partial x} - \boldsymbol{\psi}\frac{\partial T}{\partial x} = 0 \tag{8}$$

For our numerical calculations we use the stream function (φ)-vorticity (ω) formulation. These variables are introduced in the following manner: $v_x = \partial\varphi/\partial z$, $v_z = -\partial\varphi/\partial x$, $\omega = -\nabla^2\varphi$. We choose the finite-different method and explicit time scheme. For the obtaining the stream function field the Poisson equation was solved using the Jacobi iteration method. The spatial integration step was taken 30 points per unit length, $\Delta x = 1/30$, the time step was $\Delta t = \Delta x^2/32$. The tests with more accurate resolution give the difference within a couple of percent.

As the initial condition we assume the motionless state, $\varphi(x,z) = 0$, $\omega(x,z) = 0$. The temperature is supposed to be the mean temperature between the upper and lower walls, i.e. $T = 1/2$. The concentration corresponds to the homogeneous state, $C_1 = C_2 = 0$. In the dimensional variables it means the concentration components are equal to the initial mass fractions, $C_1 = C_{01} = 0.62$, $C_2 = C_{02} = 0.31$. The analysis of concentration behaviour and mass fluxes could be slightly complicated in the dimensionless formulation since when we transform concentration we multiply it by β_C, which can have different signs. Hereinafter, we imply dimensional values of the concentration field.

To bring the system out of the steady motionless state we introduce initial perturbation in the form of vorticity in the certain point ($x = 2.75$, $z = 0.75$) with the amplitude 10^{-3}.

3. Results for the two different net separation ratios

Describing the behaviour of the fluid with non-uniform distribution of density in a closed cavity we may expect the development of the convective instability or what the system would go to the mechanical equilibrium. In the case of convection it is rather difficult to anticipate a certain convection mode, but in the case of mechanical equilibrium we can make some conclusions beforehand. Let us take a look at the diffusion mass fluxes.

$$J_1 = -\rho(D_{11}\nabla C_1 + D_{12}\nabla C_2 + D_{T.1}\nabla T) \tag{9}$$

$$J_2 = -\rho(D_{21}\nabla C_1 + D_{22}\nabla C_2 + D_{T.2}\nabla T) \tag{10}$$

The mass fluxes vanish in the case of equilibrium, i.e., $J_1, J_2 = 0$. This condition yields the relation: $\nabla C_i = -S_{T,i} \nabla T$, $i = 1,2$. The temperature gradient is imposed by the problem statement and $\nabla T > 0$ (the heating from above). The Soret coefficient $S_{T,1} > 0$ (see Table 2), whence it follows that ∇C_1 must be negative. This means that C_1, toluene, is accumulating near the bottom cold wall, while the coefficient $S_{T,2} < 0$, and it should lead to a higher concentration of C_2, methanol, near the hot upper wall.

3.1. Positive net separation ratio

The final result of the direct numerical simulation in the case of the positive net separation ratio seems to be in agreement with the above discussion. However, the modeling showed some odd evolution of the diffusion process.

As we think, the component C_1 concentrates more near the bottom, but contrary to our expectations at the initial stage it goes up (see Figure 2,a). We observe the following scenario, one can split it into three steps. 1) Thermal conductivity is a much faster process than diffusion, and the temperature gradient is established soon after the start of the running. The contribution $-\rho D_{T,1} \nabla T$ to the diffusion flux (9) is >0, which means it drives the concentration up. 2) The accumulation of component C_1 near the top results in $-\rho D_{11} \nabla C_1 < 0$, i.e. the diffusion starts driving the concentration itself back to the bottom. The contribution of cross-diffusion does the same thing, $-\rho D_{12} \nabla C_2 < 0$. 3) At some moment the term $-\rho D_{11} \nabla C_1$ becomes positive, because the concentration gradient turns negative, i.e. this component goes to the lower cold wall and we observe what we expected to see since the beginning. In the end, the system takes some time to finally balance the all three contribution and the mass flux $J_1 = 0$. We may note, components experience greater impact near the walls, and the above description is valid inside the cavity.

The diffusion dynamics of the second component, C_2, however, demonstrates much more straightforward behavior (see Figure 2,b). It can be easily explained by the fact that the absolute value of the Soret coefficient in this case is almost twice larger, i.e. the thermal diffusion is twice stronger here. At the same time, the diffusion and cross-diffusion confidents are noticeably weaker in comparison with the component C_1. In other words, for the component C_2 the thermal diffusion contribution obviously dominates. This contribution is quickly established, and the diffusion development of the second component is quite predictable.
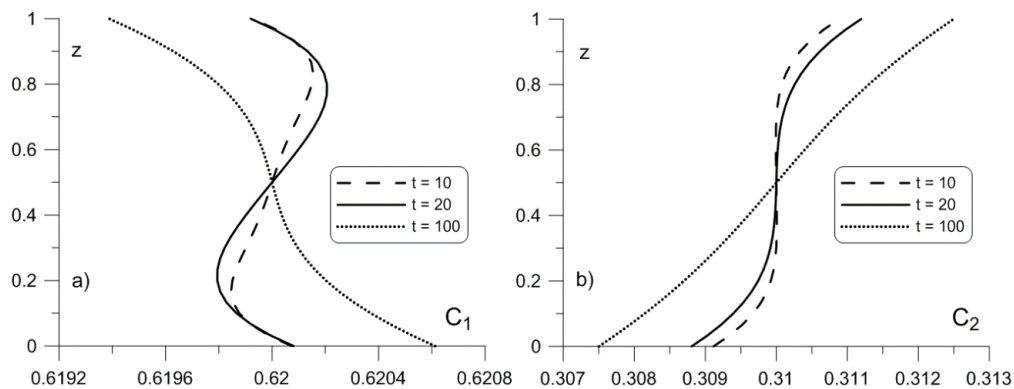

Figure 2. The component distribution with the height at different time moments.
a) toluene C_1, b) methanol C_2.

3.2. Negative net separation ratio
We found in the case of the negative net separation ratio the system development can follow two ways. We remind, to bring the system out of the steady state (which could either stable or unstable) we introduce the initial perturbation in the form of vortex at the fixed point. Our numerical calculations carried out showed, that under small magnitudes of the initial perturbation (less than $6 \cdot 10^{-5}$) the system

goes to the mechanical equilibrium, and the scenario is also similar. Accordingly, when the perturbations are higher than this threshold, we observe the development of instability. After a short initial period the system comes to the regimes with one vortex along the cavity. In figure 3 you can see the final distribution of toluene C_1, the distribution of other components look in the similar way. This is a steady state regime, which is not transformed to any other regimes with time.
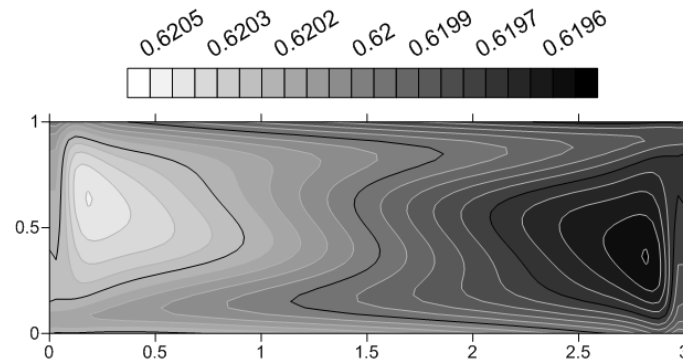

Figure 3. The final distribution of component C_1 in the case of convection instability when the net separation ratio is negative.

To understand the phenomena discussed above, we should make a remark, why the net separation ratio, Ψ, is such an important parameter. Let us take a look at expressions (11)-(12). The terms $-\beta_T \nabla T$ and $-\beta_{C1} \nabla C_1 - \beta_{C2} \nabla C_2$ are the thermal and concentration contributions to the density gradient. The physical sense of the net separation ratio is the ratio between the buoyancy forces caused by the temperature and ones caused by the gradients of concentration.

$$\Psi = \psi_1 + \psi_2 = -\frac{\beta_{C1}}{\beta_T}S_{T1} - \frac{\beta_{C2}}{\beta_T}S_{T2} = \frac{\beta_{C1}}{\beta_T}\frac{\nabla C_1}{\nabla T} + \frac{\beta_{C2}}{\beta_T}\frac{\nabla C_2}{\nabla T} = \frac{1}{\beta_T \nabla T}(\beta_{C1}\nabla C_1 + \beta_{C2}\nabla C_2) \quad (11)$$

$$\nabla \rho = \rho_0(-\beta_T \nabla T - \beta_{C1}\nabla C_1 - \beta_{C2}\nabla C_2) \quad (12)$$

We can conventionally classify contributions of the density gradient into stable and unstable ones. The term $-\beta_T \nabla T$ is < 0, i.e. the density decreases from the bottom to the top due to this part, and it gives us the stable stratification. The term $-\beta_{C1} \nabla C_1$ is also negative and plays the stabilizing role, while the term $-\beta_{C2} \nabla C_2$ is adverse. We should note, the temperature contribution exceeds others by more than an order of magnitude, in other words, the density stratification is always stable in our system. However, this fact is not sufficient for the convective stability [12]. We may observe instability even if the whole gradient is stable, which could be explained by the large difference between typical thermal and diffusion times. If $\Psi < 0$, the total concentration contribution of both components is unstable, i.e. $-\beta_{C1} \nabla C_1 - \beta_{C2} \nabla C_2 > 0$. At the bottom we have a "lighter" mixture, and an element of mixture, which accidentally moves upward, quickly takes the ambient temperature, but slowly diffuses and continues going upward. Thus, the convective instability arises. The typical diffusion times are related as $\tau_{D2}/\tau_{D1} \approx 2.7$, both components "work together", whereas the thermal time is much faster, $\tau_{D1}/\tau_T \approx 46$, $\tau_{D2}/\tau_T \approx 125$. In the opposite case, $\Psi > 0$, the "united" concentration contribution is stable, as well as the thermal one, and the equilibrium is observed, as expected.
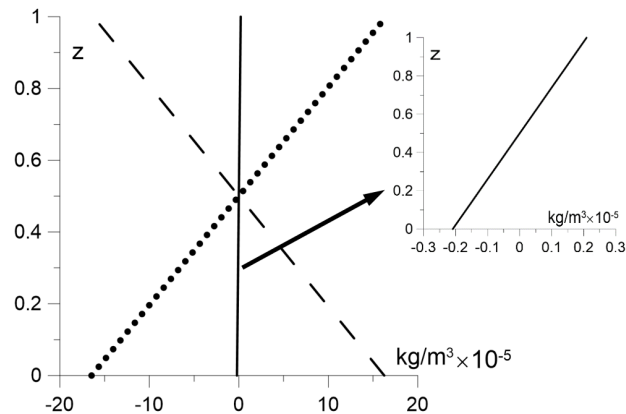
Figure 4. Concentration contributions to the density distribution. The dash line is $-\beta_{C1}(C_1 - C_{10})$, the dot line is $-\beta_{C2}(C_2 - C_{20})$, and the solid line is their sum.

4. Conclusion

We have investigated numerically the behaviour of the ternary liquid mixture of toluene-methanol-cyclohexane for the two types of the Soret coefficients measured, namely when the combination of the Soret coefficients leads to $\Psi > 0$ and to $\Psi < 0$. We have found, the system goes to the mechanical equilibrium for the positive net separation ratio, but we observe a non-trivial diffusion evolution of component C_1, toluene, when first, contrary to expectations, this component goes upward. And only after a while it goes down, and the equilibrium is established. For the negative net separation ratio, there is a threshold value of initial perturbations. Below this value, we also observe the mechanical equilibrium and the behaviour is similar to the case of $\Psi > 0$. However, when we set the value of the initial perturbation greater than a threshold one, the system comes to the single-vortex convective mode.

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