Mixing of Two Binary Nonequilibrium Phases in One Dimension

Kjetil B. Haugen and Abbas Firoozabadi
Chemical Engineering Dept., Mason Lab, Yale University, New Haven, CT 06520

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The mixing of nonequilibrium phases has important applications in improved oil recovery and geological CO_2-storage. The rate of mixing is often controlled by diffusion and modeling requires diffusion coefficients at subsurface temperature and pressure. High-pressure diffusion coefficients are commonly inferred from changes in bulk properties as two phases equilibrate in a PVT cell. However, models relating measured quantities to diffusion coefficients usually ignore convective mass transport. This work presents a comprehensive model of mixing of two nonequilibrium binary phases in one-dimension. Mass transport due to bulk velocity triggered by compressibility and nonideality is taken into account. Ignoring this phenomenon violates local mass balance and does not allow for changes in phase volumes. Simulations of two PVT cell experiments show that models ignoring bulk velocity may significantly overestimate the diffusion coefficients. *AIChE J,* 55: 1930–1936, 2009

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Introduction

For decades, fluid injection into the subsurface has been performed for a number of reasons including liquid waste deposition, natural gas storage, and improved oil recovery. For instance, the petroleum industry uses gas injection to prevent reduction in reservoir pressure.[1] Depending on the conditions, a substantial amount of the gas may dissolve in the crude, triggering secondary recovery mechanisms due to change in fluid properties. In fractured reservoirs, this may lead to significant improvements in oil recovery. When dissolution does not occur, gas injection into such reservoirs quickly flushes the oil through the fractures and an early breakthrough is observed at the production wells. Any subsequent oil production is due to gravity drainage. However, when the gas dissolves in the oil and changes its viscosity, surface tension, and density, a larger fraction of the oil in the rock matrix may become accessible for production.[2] Efficient production from fractured reservoirs requires an accurate description of how different gases affect crude properties, to what extent the gas will dissolve at reservoir conditions, and the rate at which dissolution takes place.

Increased awareness of global warming has lead to an interest in geological CO_2-storage. The most promising geological formation for large scale CO_2-storage is saline aquifers.[3] As water density increases upon CO_2-dissolution, CO_2-saturated water sinks and triggers natural convection. Generally, this is a desired effect, as natural convection increases mixing and thus the rate at which CO_2 can be injected. The density increase also means there will be no leaks through fractures sufficiently far away from the injection site. Being able to predict the rate of CO_2-dissolution in water is crucial to properly assess the storage capacity of saline aquifers.

Clearly, there are both financial and environmental incentives to study the mixing between two nonequilibrium fluid phases. Mass transfer between two fluid phases occurs by evaporation and condensation across their interface. However, because these processes are generally much faster than the diffusive and convective time scales in either phase, the

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Additional Supporting Information may be found in the online version of this article.

Correspondence concerning this article should be addressed to A. Firoozabadi at abbas.firoozabadi@yale.edu rate of mass transfer is controlled by how effectively mass is transported from the interface and into the bulk. When the density of the heavier (lighter) phase does not increase (decrease) during the mixing process, there will be no natural convection and the rate of mixing is governed by diffusion. However, diffusion induces bulk velocity and convective mass transfer may still be important.

A quantitative description of the mixing process requires diffusion coefficients. Measuring diffusion coefficients at high pressures and temperatures is a real challenge. Conventional methods rely on compositional analysis and are expensive, time-consuming, and labor-intensive. Moreover, some of the assumptions made for the models used to obtain diffusion coefficients from measurements may not be valid at high pressures. As a result, there are significant differences between diffusion coefficients reported in the literature.[4]

An attractive and powerful alternative for measuring high-pressure diffusion coefficients is the PVT cell technique in which two nonequilibrium phases are allowed to interact inside a cell at constant temperature. With proper description of the dissolution and evaporation processes, diffusion coefficients can be inferred from changes in bulk properties such as total mass, pressure, and phase volumes. The technique can be divided into three groups according to the imposed experimental conditions. In one approach, cell volume is fixed and pressure is kept constant by injecting gas at the top of the cell. Diffusion coefficients are obtained from the amount of injected gas as a function of time.[5,6] Another approach is to use a closed cell of a fixed volume. The total mass in the system is constant and diffusion coefficients are inferred from the observed changes in pressure and/or liquid volume.[4] Finally, a closed cell of varying height can be used. Either the cell works like a piston or mercury is injected into (removed from) a layer below the heavier phase. The purpose is to keep pressure constant. As in the previous approach, the total mass inside the cell is constant and diffusion coefficients are extracted from changes in phase volumes.[7]

In this work, we present an algorithm to describe nonequilibrium mass transport between the gas and liquid phases of a binary mixture in a closed PVT cell of fixed volume. It is assumed that the density gradient is always parallel to gravity. Thus, natural convection does not occur. However, convective mass transport due to compressibility and nonideality is accounted for. The significance of bulk velocity even in the absence of natural convection has been recognized in the early works of Pomeroy et al.[5] and Reamer et al.[6] However, more recent articles do not consider bulk mass transport in the modeling of PVT cell experiments.[4,7–9] In the closely related problem of evaporation of a volatile liquid from an open container, Slattery[10] demonstrates that bulk mass transport is not negligible and that the importance increases with gas solubility. His analysis is limited to gas and liquid phases with constant molar volume and is not applicable to nonideal mixtures.

The article is organized along the following. After formulating the problem and presenting the boundary conditions, we use local mass balance to relate bulk velocity to the rates of change in pressure and composition. Then, we introduce the equations for chemical equilibrium and mass and component balance across the interface. The result section investigates the effect of bulk mass transport on the mixing of gas and liquid phases in two different binary mixtures. The details of the numerical solution procedure are provided in the Supporting Information.

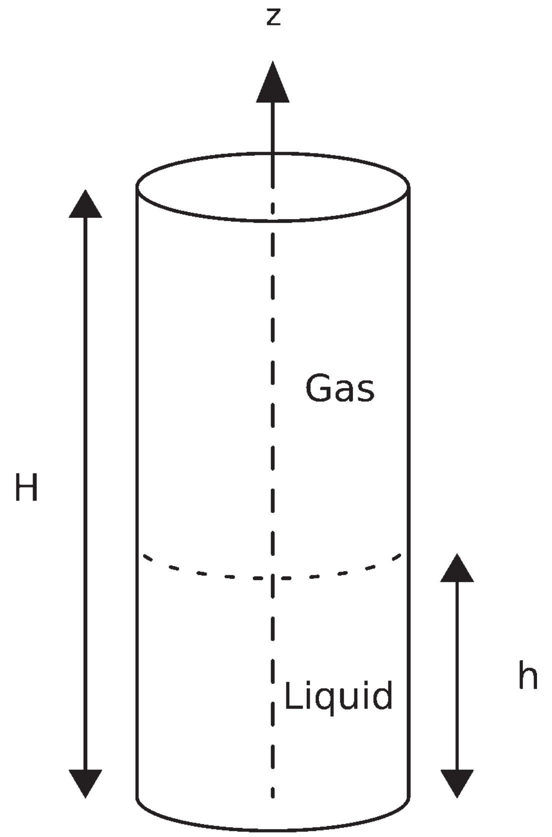

Figure 1. A sketch of a cylindrical PVT cell of height *H* filled with a gas and a liquid.

The liquid level is denoted by h. Also shown is the coordinate axis z.

Problem Formulation and Key Assumptions

We simulate experiments conducted in a cylindrical PVT cell of height H (see Figure 1). The cell is filled by a liquid to a desired level $h = h_0$ and subsequently pressurized by a gas until the desired initial pressure $P = P_0$ is reached. The entire process of filling the cell is short compared with the duration of the experiment and we assume mass transfer between the phases to be negligible during this time. Initially, the interface between the gas and liquid phases is located at $z = h_0$, where z is the vertical coordinate centered at the bottom of the cell. The two phases exchange mass as they equilibrate and as a result, the pressure P and liquid level h in the cell vary with time t.

We employ the concept of local thermal, mechanical, and chemical equilibrium both in the bulk phases and at their interface. The latent heat produced (absorbed) in the dissolution (evaporation) process is withdrawn (supplied) by conduction. In pure fluids, the phase change is controlled by the rate at which the heat transfer occurs, and the process is clearly nonisothermal. However, in a number of problems on phase change in mixtures, evaporation and dissolution are limited by the rate at which the components are transported between the interface and the bulk. Provided the cell radius is sufficiently small, phase change in a PVT cell is indeed controlled by mass transport, and the experiment can regarded as isothermal.

Only mixtures in which liquid density decreases with dissolution and gas density increases with evaporation are considered. Thus, there is no natural convection and the problem is one-dimensional. The absence of natural convection justifies ignoring the momentum balance. Although gravity and viscous stress will lead to local pressure gradients, the spatial variations in pressure are negligible compared to the overall pressure drop. Consequently, we assume a uniform pressure P throughout the cell. This also means that pressure is continuous through the interface, implying that the radius of the cell is large enough to avoid a curved interface.

All boundaries are considered impermeable, and both bulk velocities v and diffusive fluxes J must vanish at the top and bottom boundaries,

$$\begin{aligned} v^{\mathrm{G}} &= 0, \quad z = H, \\ v^{\mathrm{L}} &= 0, \quad z = 0, \end{aligned} \tag{1}$$

$$\begin{aligned} J^{\mathrm{G}} &= 0, \quad z = H, \\ J^{\mathrm{L}} &= 0, \quad z = 0, \end{aligned} \tag{2}$$

where G and L denote the gas and liquid phases, respectively. In this work, we express diffusive flux by Fick's law. In a binary mixture, the diffusive flux of either component is given by

$$J = -cD\frac{\partial n}{\partial z}, \tag{3}$$

where c is molar density, D is the molecular diffusion coefficient, and n is mole fraction. Consequently, the no-flux boundaries imply vanishing composition gradients, i.e.,

$$\begin{aligned} \frac{\partial n^{\mathrm{G}}}{\partial z} &= 0, \quad z = H, \\ \frac{\partial n^{\mathrm{L}}}{\partial z} &= 0, \quad z = 0. \end{aligned} \tag{4}$$

Local Mass Balance

In the absence of natural convection, bulk velocity is uniquely determined by local mass balance,

$$\frac{\partial c}{\partial t} + \frac{\partial}{\partial z}(cv) = 0. \tag{5}$$

Clearly, a change in local molar density must lead to bulk velocity. We are not aware of any investigation of the influence of bulk velocity on the analysis of PVT cell experiments. As the temperature in the cell is constant, molar density is a function of pressure and composition only. Using the chain rule, we get

$$c\frac{\partial v}{\partial z} = -\frac{\partial c}{\partial n}\left(\frac{\partial n}{\partial t} + v\frac{\partial n}{\partial z}\right) - \frac{\partial c}{\partial P}\left(\frac{\partial P}{\partial t} + v\frac{\partial P}{\partial z}\right). \tag{6}$$

Combining Eq. (6) with the expression for local component balance,

$$c\left(\frac{\partial n}{\partial t} + v\frac{\partial n}{\partial z}\right) = -\frac{\partial J}{\partial z}, \tag{7}$$

and recalling that the pressure gradients are assumed negligible, the velocity gradient in either phase is determined by

$$\frac{\partial v}{\partial z} = \frac{1}{c^2}\frac{\partial c}{\partial n}\left(\frac{\partial J}{\partial z}\right) - \frac{1}{c}\frac{\partial c}{\partial P}\frac{\partial P}{\partial t}. \tag{8}$$

Gas (liquid) velocities are readily obtained by integrating Eq. (8) from the top (bottom) boundary,

$$v^{\mathrm{G}}(z) = -\int_z^H \frac{1}{(c^{\mathrm{G}})^2}\frac{\partial c^{\mathrm{G}}}{\partial n^{\mathrm{G}}}\left(\frac{\partial J^{\mathrm{G}}}{\partial z}\right)dz' + \frac{\partial P}{\partial t}\int_z^H \frac{1}{c^{\mathrm{G}}}\frac{\partial c^{\mathrm{G}}}{\partial P}dz', \quad h(t) \le z \le H, \tag{9a}$$

$$v^{\mathrm{L}}(z) = \int_0^z \frac{1}{(c^{\mathrm{L}})^2}\frac{\partial c^{\mathrm{L}}}{\partial n^{\mathrm{L}}}\left(\frac{\partial J^{\mathrm{L}}}{\partial z}\right)dz' - \frac{\partial P}{\partial t}\int_0^z \frac{1}{c^{L}}\frac{\partial c^{\mathrm{L}}}{\partial P}dz', \quad 0 \le z \le h(t). \tag{9b}$$

Note that there are two sources of local density change. That is, nonideality, leading to change in volume on mixing, and compressibility. In general, nonideality dominates in the liquid phase, whereas compressibility dominates in the gas phase.

Conditions at the Interface

As mentioned in the problem formulation, we assume local chemical equilibrium. In the bulk phases, this is guaranteed by continuous variations in composition. At the interface, where there is a jump in composition, we require the fugacity f_j of component j to be the same in both phases,

$$\ln f_j^{\mathrm{G}}(T, P, n^{\mathrm{G}}) = \ln f_j^{\mathrm{L}}(T, P, n^{\mathrm{L}}), \quad j = 1, 2, \quad z = h(t). \tag{10}$$

Note that for a given temperature and pressure, Eq. (10) represents two equations in two unknowns. Thus, in a binary mixture, interfacial composition is a function of temperature and pressure only.

As mass is neither created nor destroyed, flux must be continuous everywhere, also across the interface. The fact that the interface is moving must be taken into account. The expression for component balance across the interface is

$$c^{\mathrm{G}}n_j^{\mathrm{G}}\left(v^{\mathrm{G}} - \frac{\partial h}{\partial t}\right) + J_j^{\mathrm{G}} = c^{\mathrm{L}}n_j^{\mathrm{L}}\left(v^{\mathrm{L}} - \frac{\partial h}{\partial t}\right) + J_j^{\mathrm{L}}, \quad j = 1, 2 \quad z = h(t). \tag{11}$$

(For the sake of completeness, the derivation is presented in Appendix A of the Supporting Information material)

Table 1. Experimental Conditions for the Two PVT Cell Experiments

	C_1-nC_5	C_1-nC_{12}
T (°C)	37.8	65
H (cm)	21.94	10.00
h_0 (cm)	7.68	2.00
P_0 (MPa)	10.2	23.4

The cell has height H and operates at a constant temperature T. The initial values of liquid level h and pressure P are also reported.

Keeping in mind that the sum of the mole fractions equals unity and that the sum of diffusive fluxes is equal to zero, the expression for total mass balance is readily obtained by summing Eq. (11) over both components,

$$c^{G}\left(v^{G}-\frac{\partial h}{\partial t}\right)=c^{L}\left(v^{L}-\frac{\partial h}{\partial t}\right),\quad z=h(t). \tag{12}$$

Rearranging Eq. (12), we can see that a moving interface requires for the bulk velocity of at least one of the phases to be nonzero at the interface,

$$c^{L}v^{L}-c^{G}v^{G}=\left(c^{L}-c^{G}\right)\frac{\partial h}{\partial t},\quad z=h(t). \tag{13}$$

Results

The above set of equations is solved numerically. The details of the numerical algorithm are outlined in Appendices B and C of the Supporting Information material. To verify the model and to investigate the importance of bulk mass transport on the mixing of the phases, we simulated two PVT cell experiments performed with methane–pentane (C_1-nC_5) and methane–dodecane (C_1-nC_{12}) mixtures, respectively. In both cases, the gas phase is initially pure methane, and the liquid phase is pure in the heavy component. Composition is always specified by the mole fraction of methane. Cell height, temperature, and initial conditions for both simulations are listed in Table 1. Fugacity and mixture properties are calculated from the Peng-Robinson equation of state.[11] Relevant component data are provided in Table 2.

Quantifying the Effect of Bulk Mass Transport

In the proposed algorithm, the rates of change in pressure, liquid level, and composition depend on bulk phase velocity. To quantify the importance of bulk mass transport, we also developed an algorithm in which all convective terms are neglected. Note that such a formulation is inconsistent with a change in local density and violates local mass balance. Moreover, no bulk flow is also inconsistent with a change in liquid level [see Eq. (13)]. Nevertheless, no bulk flow is a common assumption in the modeling of PVT cell experiments.

Comparing simulations with the two different versions of the code, we can evaluate the error introduced by ignoring bulk mass transport. Note that changes in pressure and liquid level can no longer be calculated as outlined in Appendix C of the Supporting Information material. Instead, at each time step, pressure, liquid level, and interfacial composition are determined by solving the isofugacity equations in Eq. (10) under the constraint of global mass balance,

$$\int_{0}^{h(t)} c^{L}dz+\int_{h(t)}^{H} c^{G}dz=\text{const.} \tag{14}$$

$$\int_{0}^{h(t)} c^{L}n^{L}dz+\int_{h(t)}^{H} c^{G}n^{G}dz=\text{const.} \tag{15}$$

Methane–Pentane Mixture

Riazi[4] developed one of the more comprehensive models of PVT cell experiments in the literature and tested it on a methane–pentane mixture. As a verification of our model, we simulate the evolution of pressure and liquid level for the same experiment. Conditions are chosen to match those provided by Riazi. We also use the reported binary interaction coefficient of 0.054 when calculating mixture properties from the Peng-Robinson equation of state.[11] Riazi's model allows for time dependent diffusion coefficients and estimates the diffusion coefficient in each phase from a spatial average of the values predicted by the Riazi-Whitson correlation.[13] Our model implements both spatial and temporal variations in the diffusion coefficients. In the current implementation of our code, the correlation from Leahy-Dios and Firoozabadi[14] is used. However, varying diffusion coefficients makes it more difficult to identify the contribution from bulk mass transport. Thus, we use only constant values in the following. Based on the diffusion coefficients reported by Riazi, we choose $D^{G}=1.0\times10^{-7}$ m^2 s^{-1} and $D^{L}=1.3\times10^{-8}$ m^2 s^{-1}.

Figure 2 shows the measured pressure drop as well as the predictions obtained by fitting our model (solid line) and Riazi's model (dashed line) to the experimental data. Both models provide excellent predictions of the observed pressure drop although Riazi's model suffers from a slight undershoot about 50 h into the simulation. Note that the measured pressure eventually falls somewhat below the predicted values. This may be due to a minor deficiency in the cubic equation of state used in this work or due to a small leak in the PVT cell.

Figure 3 illustrates how the pressure drop is influenced by bulk mass transport. This effect is not accounted for in Riazi's model. Our model (solid line) predicts the pressure drop very well. However, if bulk mass transport is ignored (dashed line), the predicted drop in pressure occurs more

Table 2. Input Parameters for the Peng-Robinson Equation of State[11]

	T_C (K)	P_C (MPa)	ω	s
C_1	190.6	4.54	0.008	−0.154
nC_5	469.7	3.37	0.251	−0.042
nC_{12}	658.1	1.82	0.574	0.115

Critical temperatures (T_C) and pressures (P_C), and acentric factors (ω) are from NIST Chemistry WebBook (http://webbook.nist.gov/chemistry). Volume shift parameters (s) are from Jhaveri and Youngren.[12]

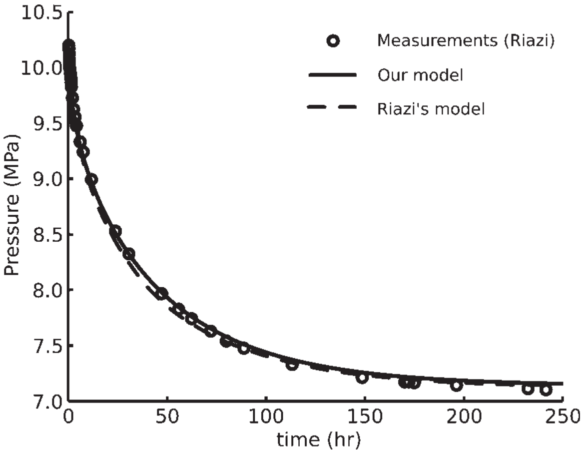

Figure 2. A comparison of the measured and predicted pressure drops for the methane–pentane mixture.[4]

In Riazi's model, diffusion coefficients are obtained from a modified version of the Riazi-Whitson correlation.[13] In our model, we use constant diffusion coefficients of $D^L = 1.3 \times 10^{-8}$ m^2 s^{-1} and $D^G = 1.0 \times 10^{-7}$ m^2 s^{-1}.

slowly. Conclusively, bulk mass transport leads to an increased rate of mixing. The observed pressure decay can be captured by the purely diffusive model if a somewhat larger liquid diffusion coefficient is used (dotted line).

Riazi does not report measurements of the increase in liquid level. However, as bulk mass transport increases mixing, the predicted rate of increase is higher for our model than for the purely diffusive model (see Figure 4). The two models agree if a larger liquid diffusion coefficient is used when bulk mass transport is ignored.

Methane–Dodecane Mixture

As the liquid phase is virtually incompressible, liquid bulk velocity is mainly the result of change in volume on mixing. Thus, the importance of bulk mass transport in the liquid should increase with nonideality and gas solubility. As an illustration, we simulate a PVT cell experiment with one of the methane–dodecane mixtures studied by Jamialamhadi et al.[7] Because of high pressure (see Table 1), a substantial amount of methane dissolves in the liquid phase. The reported liquid diffusion coefficient $D^L = 1.3 \times 10^{-8}$ m^2 s^{-1} is identical to the one we used for the methane–pentane mixture above. As dodecane is virtually nonvolatile, there is hardly any diffusion in the gas phase. Thus, the simulation is insensitive to the value of the gas diffusion coefficient, and we choose to use $D^G = 1.0 \times 10^{-7}$ m^2 s^{-1}. In the simulation, we use a binary interaction coefficient (0.034) determined from experimental vapor-liquid equilibrium data.[15]

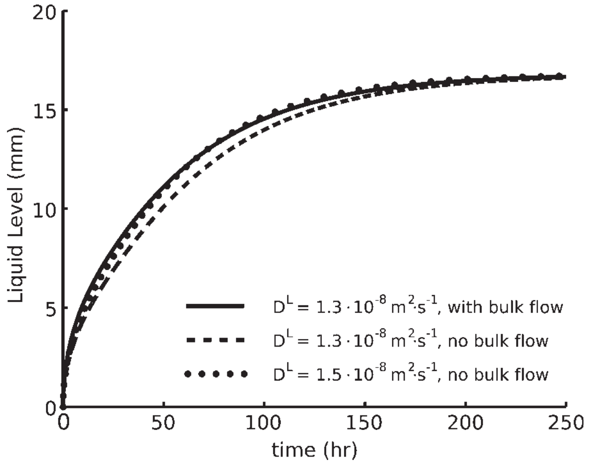

Figure 4. An illustration of how the liquid level increase in the methane–pentane mixture[4] is influenced by bulk mass transport.

The higher rate of liquid level increase can be captured by a purely diffusive model if a larger effective diffusion coefficient is used.

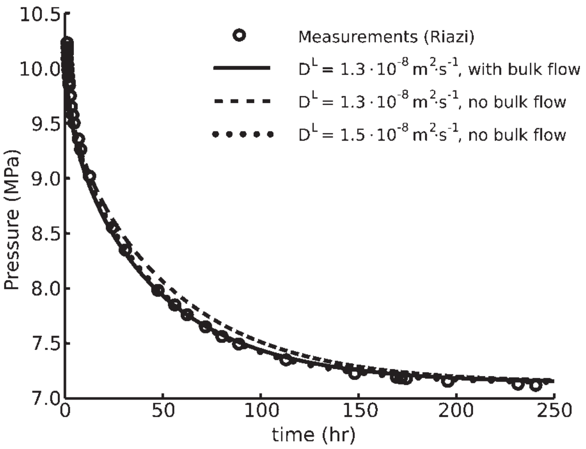

Figure 3. An illustration of how the pressure drop in the methane–pentane mixture[4] is influenced by bulk mass transport.

The higher rate of pressure decrease can be captured by a purely diffusive model if a larger effective diffusion coefficient is used.

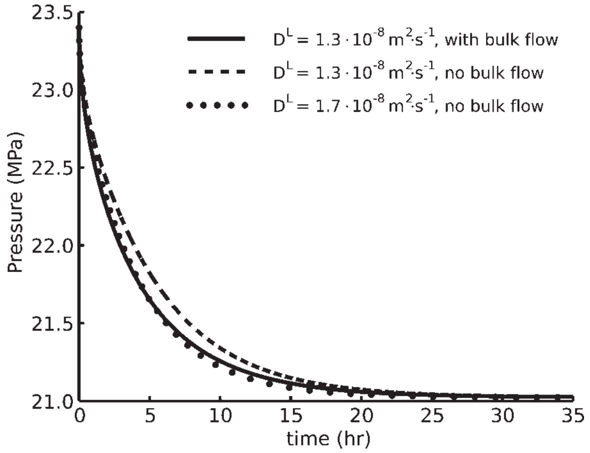

Figure 5. An illustration of how the pressure drop in the methane–dodecane mixture[7] is influenced by bulk mass transport.

The higher rate of pressure decrease can be captured by a purely diffusive model if a larger effective diffusion coefficient is used.

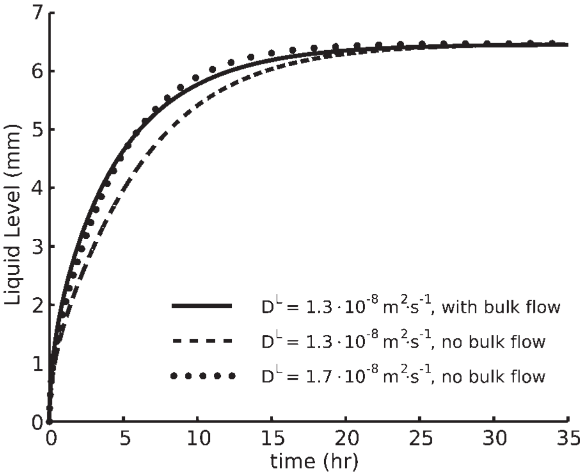

Figure 6. An illustration of how the liquid level increase in the methane–dodecane mixture[7] is influenced by bulk mass transport.

The higher rate of liquid level increase can be captured by a purely diffusive model if a larger effective diffusion coefficient is used.

Note that Jamialahmadi et al.[7] kept the pressure constant by continuously adjusting the size of their PVT cell. Consequently, a direct comparison between their measurements and the results of our simulations is not provided. In the simulations, a fixed cell height of $H = 10.00$ cm and an initial liquid level of $h_0 = 2.00$ cm are used. The small liquid volume fraction keeps the pressure from dropping more than 10% below its initial value.

Figures 5 and 6 show the same trend as observed for the methane–pentante mixture. The rates of change in pressure and liquid level are higher when bulk velocity is taken into account. The predictions by the two models are very similar if a larger liquid diffusion coefficient is used when bulk mass transport is ignored. However, although an increase of about 15% was sufficient for the methane–pentane mixture, the methane–dodecane mixture requires an increase of about 30%.

Concluding Remarks

In general, bulk mass transport cannot be ignored when describing one-dimensional mixing of gas and liquid phase in a PVT cell. In fact, in the gas phase, high compressibility makes convection the dominant mass transport mechanism. As can be seen in Figure 7, the contribution from gas diffusion is negligible when the liquid phase is virtually nonvolatile. Liquids are essentially incompressible, but can be much more nonideal than gases. At high pressures where the limit of solubility is significant, change in volume on mixing generates bulk flow which leads to nonnegligible convective mass transport. Figure 7 shows that convective flux in the liquid phase is more important for the methane–dodecane mixture where methane solubility is higher. Nevertheless, the observed changes to pressure and liquid level can be described very well with a purely diffusive model as long as a higher liquid diffusion coefficient is used. This is because bulk velocity is completely diffusion driven and, thus, both convective and diffusive mass transport exhibit similar time dependencies. For the methane–pentane and methane–dodecane mixtures studied in this work, the results show that a purely diffusive description of the process overestimates the liquid diffusion coefficient by 15% and 30%, respectively.

For the sake of brevity we have not included examples which show the effect of bulk phase velocity on the

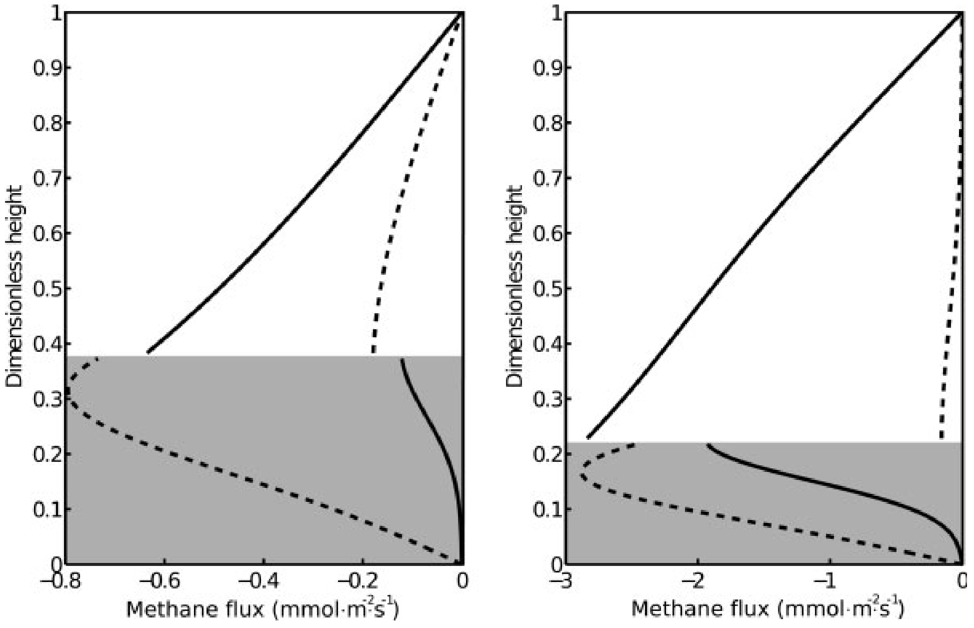

Figure 7. Two snapshots showing methane flux in the gas (white) and liquid (grey) phases of the methane–pentane (left) and methane–dodecane (right) mixtures.

Convective (solid) and diffusive (dashed) fluxes are shown separately. The snapshots are taken at the same dimensionless time $t/\tau = 0.1$ where characteristic time is calculated from liquid diffusion coefficients D^L and initial liquid level h_0, i.e., $\tau = h_0^2/D^L$.

estimation of gas phase diffusion coefficients. When the liquid phase is virtually nonvolatile, gas diffusion is negligible and the corresponding diffusion coefficient cannot be found from PVT cell experiments. However, our algorithms can also be applied when the liquid phase is volatile. Gas diffusion is no longer negligible and provided the gas still dissolves in the liquid, one can explore proper estimation of both gas and liquid diffusion coefficients.

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Notation

c = molar density
D = molecular diffusion coefficient
f = fugacity
H = cell height
h = liquid level
J = mole flux
N = Number of nodes in bulk phase
n = mole fraction
P = pressure
s = volume shift parameter
T = temperature
t = time
v = mole averaged velocity
z = vertical coordinate
ω = acentric factor
τ = characteristic time

Subscripts

0 = initial value
C = critical property

Superscripts

G = gas phase
L = liquid phase

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