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Liquid-Phase Mutual Diffusion Coefficients for Athabasca Bitumen + Pentane Mixtures

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The liquid-phase mutual diffusion coefficients for Athabasca bitumen (1) + pentane (2), determined by a free diffusion method, and subsequent analyzing the composition profiles established by X-ray transmission tomography are reported at 295 K. Particular care was taken in the analysis of composition profiles. A method that accounts explicitly for the variation of mutual diffusion coefficient and density with liquid composition was employed in order to obtain time-independent diffusion coefficients consistent with relevant theories and exogenous data sets for mutual diffusivities in liquids.

Introduction

Liquid-phase mutual diffusion coefficients are important parameters describing oil and gas reservoirs as they help define the time scale for secondary recovery processes such as miscible flooding with carbon dioxide or alkanes and consequently their economic viability. Normally, oil + flooding fluid mixtures are treated as pseudo-binaries for the purpose of mutual diffusion coefficient determination, where the oil is lumped and the added hydrocarbon or carbon dioxide, for example, comprise the second component. Mutual diffusion coefficients are not measured directly but are inferred from experimental data. Diverse experimental methods and data interpretation techniques including computation of diffusion coefficients from measured concentration profiles are employed.[1−3] The key experimental challenges with heavy oils/bitumen are that they are opaque to visible light, possess large variations of density with composition, and include high concentrations of asphaltenes or other strongly associating and surface active materials. Many conventional techniques for measuring concentration profiles, such as refractive index, or for analyzing data to obtain diffusion coefficients are not applicable. These latter issues are addressed in a companion paper.[4] In this contribution, X-ray transmission tomography is used to establish accurate composition profiles within the liquid phase, and a data analysis method that accounts explicitly for the variation of mutual diffusion coefficient and density with composition is employed.

Experimental Section

The mutual diffusion coefficients for Athabasca bitumen (1) + pentane (2) were measured at (295 ± 0.5) K and atmospheric pressure $p \approx 0.1$ MPa using a free diffusion method, where a cylindrical glass tube (internal diameter 37 mm, length 130 mm) was employed as a diffusion column in which 38 cm^3 of anhydrous pentane ($w = 0.99 +$) was injected on top of 42 cm^3 of bitumen. Reported densities and viscosities for Athabasca bitumen are 1000 $\text{kg}\cdot\text{m}^{-3}$ and ≈ 18 Pa·s, respectively, at 297 K. Initially, a sharp boundary was evident between the pentane and bitumen (see Figure 1). The composition changes that occurred in the vicinity of the original boundary were then followed by measuring the time and spatial variations of the transmitted X-ray intensity. A detailed description of this X-ray view-cell technique is available elsewhere.[5,6] Briefly, the technique resembles standard view-cell technologies except that polychromatic X-rays are transmitted through the view-cell instead of visible or infrared light. The local intensity of a transmitted X-ray image (I) depends on the absorbance (μ), density (ρ), and thickness of the sample (Δx) for a fixed incident intensity (I_0) as shown in

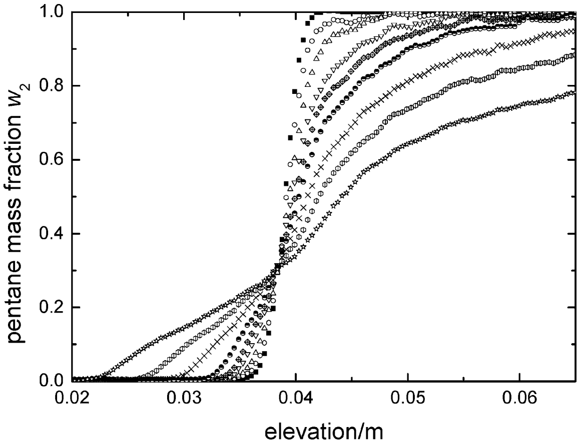

Figure 1. Composition profiles for Athabasca bitumen (1) + pentane (2) at 295 K. Diffusion time is a parameter. ■, 180 s; ○, 1800 s; △, 5400 s; ▽, 12600 s; ◇, 19800 s; ◓, 37800 s; ⬡, 88200 s; ×, 174600 s; ☆, 347400 s.

$$I = I_0 e^{-\rho \Delta x \mu} \qquad (1)$$

With calibration, absolute phase densities can be determined to within 1 $\text{kg}\cdot\text{m}^{-3}$. In this study, the local transmitted intensities for both bitumen and pure pentane define background calibrations for transmitted intensities falling between these two values. If we assume that there is no volume change during the free diffusion process, then the local mass fraction w_2 of pentane at any elevation is simply related to the calibrated local transmitted intensity measurements:

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$$w_2 \approx \ln\left(\frac{I}{I_1}\right)/\ln\left(\frac{I_2}{I_1}\right) \qquad (2)$$

Composition profiles (Figure 1) were constructed by digitizing transmitted X-ray video images of the liquid in the glass tube. Data acquisition times per profile were less than 0.1 s. Individual composition measures reflect intensities averaged over the height of one pixel (385.6 μm) and the width of 38 pixels (14.6 mm). Composition profiles were smoothed prior to analysis.

Computation of Diffusion Coefficients: Analysis of Composition Profiles

The fundamental equations related to diffusion and their derivation are available from numerous sources for diverse contexts. Two pertinent standard reference texts include Bird et al.[7] and Poling et al.[8] Only key aspects of the defining equations are repeated here. The equation of continuity for a binary mixture in the absence of chemical reaction and bulk flow, where mass transfer occurs in only one direction, is given by

$$\frac{\partial(\rho(w_2)w_2(x,t))}{\partial t} = \frac{\partial}{\partial x}\,\rho(w_2)D_{12}(w_2)\frac{\partial w_2(x,t)}{\partial x} \qquad (3)$$

where x is the spatial coordinate, t is time, D_{12} is the mutual diffusion coefficient, w_2 is the fraction of the flooding fluid (pentane), and ρ is density. Expansion of eq 3 to allow for the variation of density and diffusivity with composition yields

$$\frac{\partial w_2}{\partial t}\left(\rho + w_2\frac{\partial \rho}{\partial w_2}\right) = D_{12}\left[\frac{\partial \rho}{\partial w_2}\left(\frac{\partial w_2}{\partial x}\right)^2 + \rho\frac{\partial^2 w_2}{\partial x^2}\right] + \frac{\partial D_{12}}{\partial w_2}\rho\left(\frac{\partial w_2}{\partial x}\right)^2 \qquad (4)$$

On rearrangement, one obtains the standard form for the expression of differential equations:

$$\frac{\partial D_{12}}{\partial w_2} + D_{12}\left[\frac{\partial \rho}{\partial w_2}\frac{1}{\rho} + \frac{\partial^2 w_2}{\partial x^2}\Big/\left(\frac{\partial w_2}{\partial x}\right)^2\right] = \left(1 + \frac{w_2}{\rho}\frac{\partial \rho}{\partial w_2}\right)\frac{\partial w_2}{\partial t}\Big/\left(\frac{\partial w_2}{\partial x}\right)^2 \qquad (5)$$

where the density derivative with composition and the composition derivatives with time and space are all measurable experimentally. If one asserts that the spatial and time derivatives may be described by a single joint variable, then eq 5 may be treated as a first-order ordinary differential equation in composition:

$$\frac{\partial D_{12}}{\partial w_2} + D_{12}A(w_2) = B(w_2) \qquad (6)$$

with the standard solution

$$D_{12} = \frac{\int B(w_2)\exp(\int A(w_2)\,\mathrm{d}w_2)\,\mathrm{d}w_2 + \mathrm{C}}{\exp(\int A(w_2)\,\mathrm{d}w_2)} \qquad (7)$$

where C is a constant of integration. Equation 7 is consistent with expectation and with theory (i.e., mutual diffusion coefficients are functions of composition, phase state, temperature, and pressure but not time and space). In the absence of a general theory for the dependence of mutual diffusion coefficient on composition,[8] two approaches may be adopted to obtain expressions for the mutual diffusion coefficient:

(a) One can deduce a functional form by integrating eq 7 based on series approximations of the functions A and B, where

$$A = \sum_{i=0}^{\infty} A_i w_2^i \qquad (8)$$

$$B = \sum_{i=0}^{\infty} B_i w_2^i \qquad (9)$$

On integration, one obtains a general expression

$$D_{12} \approx \exp\left[-\sum_{i=0}^{\infty}\left(\frac{A_i}{i+1}\right)w_2^{i+1}\right] \times (C + \lambda_0 w_2 + \lambda_1 w_2{}^2 + \lambda_2 w_2{}^3 + ...) \qquad (10)$$

and its derivative with composition

$$\frac{\partial D_{12}}{\partial w_2} \approx \exp\left[-\sum_{i=0}^{\infty}\left(\frac{A_i}{i+1}\right)w_2^{i+1}\right][(\lambda_0 + 2\lambda_1 w_2 + 3\lambda_2 w_2{}^2 + ...) - (\sum_{i=0}^{\infty} A_i w_2^i)(C + \lambda_0 w_2 + \lambda_1 w_2{}^2 + ...)] \qquad (11)$$

The integration of eq 7 to obtain eq 10 is approximate. While the exponential term is exact, the parameters (λ_i) appearing in the second term only arise if one expands the integrating factor $\exp(\int A(w_2)\,\mathrm{d}w_2)$ as a Taylor series to complete the integral $\int B(w_2)\exp(\int A(w_2)\,\mathrm{d}w_2)\,\mathrm{d}w_2$. Equations 10 and 11 are substituted into the objective function (eq 12), a rearrangement of eq 5, which is minimized using the composition profile data to obtain values for the coefficients A_i, λ_i, and C:

$$S = \frac{1}{n}\sum_{1}^{n}\left|\frac{\partial D_{12}}{\partial w_2} + D_{12}\left[\frac{\partial \rho}{\partial w_2}\frac{1}{\rho} + \frac{\partial^2 w_2}{\partial x^2}\Big/\left(\frac{\partial w_2}{\partial x}\right)^2\right] - \left(1 + \frac{w_2}{\rho}\frac{\partial \rho}{\partial w_2}\right)\frac{\partial w_2}{\partial t}\Big/\left(\frac{\partial w_2}{\partial x}\right)^2\right| \qquad (12)$$

where n is the number of measurements in the composition profile.

(b) Alternatively, one can express the mutual diffusion coefficient as a Taylor series in composition, where

$$D_{12} = \alpha + \beta w_2 + \epsilon w_2{}^2 + \gamma w_2{}^3 + \kappa w_2{}^4 ... \qquad (13)$$

and

$$\frac{\partial D_{12}}{\partial w_2} = \beta + 2\epsilon w_2 + 3\gamma w_2{}^2 + 4\kappa w_2{}^3 ... \qquad (14)$$

Equations 13 and 14 can be substituted into eq 12 to obtain values for the parameters α and β. As eq 13 can be obtained from eq 11 by expanding the exponential term in the form of a Taylor series, both approaches are equivalent and are expected to yield similar results.

Results and Discussion

Liquid-phase mutual diffusion coefficients D_{12} for Athabasca bitumen (1) + pentane (2) at 295 K computed from smoothed composition profiles using eqs 3 to 12 are listed in Table 1. As is clear from Figure 2, a range of estimates is still obtained for

Table 1. Liquid-Phase Mutual Diffusion Coefficients D_{12} for Athabasca Bitumen (1) + Pentane (2) at 295 K Based on Equations 3 through 12 and Smoothed Composition Profiles[a]

w_2	$10^{10}\,D_{12}$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^{10}\,\sigma^b$ / $\mathrm{m^2 \cdot s^{-1}}$	w_2	$10^{10}\,D_{12}$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^{10}\,\sigma^b$ / $\mathrm{m^2 \cdot s^{-1}}$
0.10	1.8	0.5	0.55	1.4	0.3
0.15	1.9	0.5	0.60	1.4	0.4
0.20	1.7	0.3	0.65	1.6	0.4
0.25	1.5	0.3	0.70	1.6	0.4
0.30	1.4	0.3	0.75	1.9	0.4
0.35	1.4	0.3	0.80	2.2	0.5
0.40	1.4	0.3	0.85	2.0	0.5
0.45	1.4	0.3	0.90	2.2	0.5
0.50	1.4	0.3			

[a] Reported values were averaged over all profiles measured at different times. [b] Standard deviation.

mutual diffusion coefficients at fixed composition irrespective of whether raw or smoothed data, or eqs 3 to 12 or eqs 12 to 14 are employed. However, the range of values is narrow, reflecting intrinsic errors in the underlying physical measurements, and the values are consistent with one another, with theory and with reliable exogenous measurements for liquids. The average values at each composition have standard deviations of ± 25 %. Thus, the value of the mutual diffusion coefficient is $(1.7 \pm 0.4) \cdot 10^{-10}\ \mathrm{m^2 \cdot s^{-1}}$ for Athabasca bitumen (1) + pentane (2) mixtures in the composition range $w_2 = (0.1 \text{ to } 0.9)$ at $T = 295$ K and $p \approx 0.1$ MPa. Compared to literature data for similar systems bitumen−alkane,[9,10] the mutual diffusion coefficients reported here are in the same range—$10^{-10}\ \mathrm{m^2 \cdot s^{-1}}$.

Extrapolation from $w_2 = 0.9$ to $w_2 = 1$ appears to underestimate the mutual diffusion coefficient for Athabasca bitumen at infinite dilution. Based on the dynamic viscosity of pentane at 295 K, $\eta_2 = 0.225\ \mathrm{mPa \cdot s^{-1}}$,[8] a molar mass $M_2 = 72.15\ \mathrm{g \cdot mol^{-1}}$, $\phi = 1$ (association parameter for most hydrocarbon solvents), and assuming an average molar volume for bitumen $V_1 = 1000\ \mathrm{cm^3 \cdot mol^{-1}}$, the Wilke-Chang correlation

$$D_{12}^{\infty} = \frac{7.4 \cdot 10^{-8} (\phi M_2)^{1/2} T}{\eta_2 V_1^{0.6}} \tag{15}$$

predicts a mutual limiting diffusion coefficient for infinitely dilute Athabasca bitumen in pentane $D_{12}^{\infty} \approx 1.3 \cdot 10^{-9}\ \mathrm{m^2 \cdot s^{-1}}$. Reported values for the molar volume for bitumen vary, and it is not clear what the degree of association is for this case. The mutual diffusion coefficient value indicated by Figure 2 and Table 1 is approximately one-eighth of this value. Planned changes in our experimental technique aimed at improving the spatial resolution to ≈200 μm, and the composition resolution to a mass fraction of ≈ 0.003, for smoothed values, are expected to reduce this difference as we will be able to extend the mass fraction range examinable to greater than 0.95 at short diffusion times. However, it is an open question whether or not the expected large increase in mutual diffusion coefficient at near infinite dilution can be captured using the free diffusion experimental method and the analysis method proposed here. This arises in part because of anticipated fluid behavioral changes at low concentration. Asphaltenes, for example, a key component of bitumen and heavy oil, associate strongly at concentrations as low as 50 ppm.[11] Thus, the mutual diffusivity value reported here reflects the behavior of feeds comprising aggregated species and not just molecules.

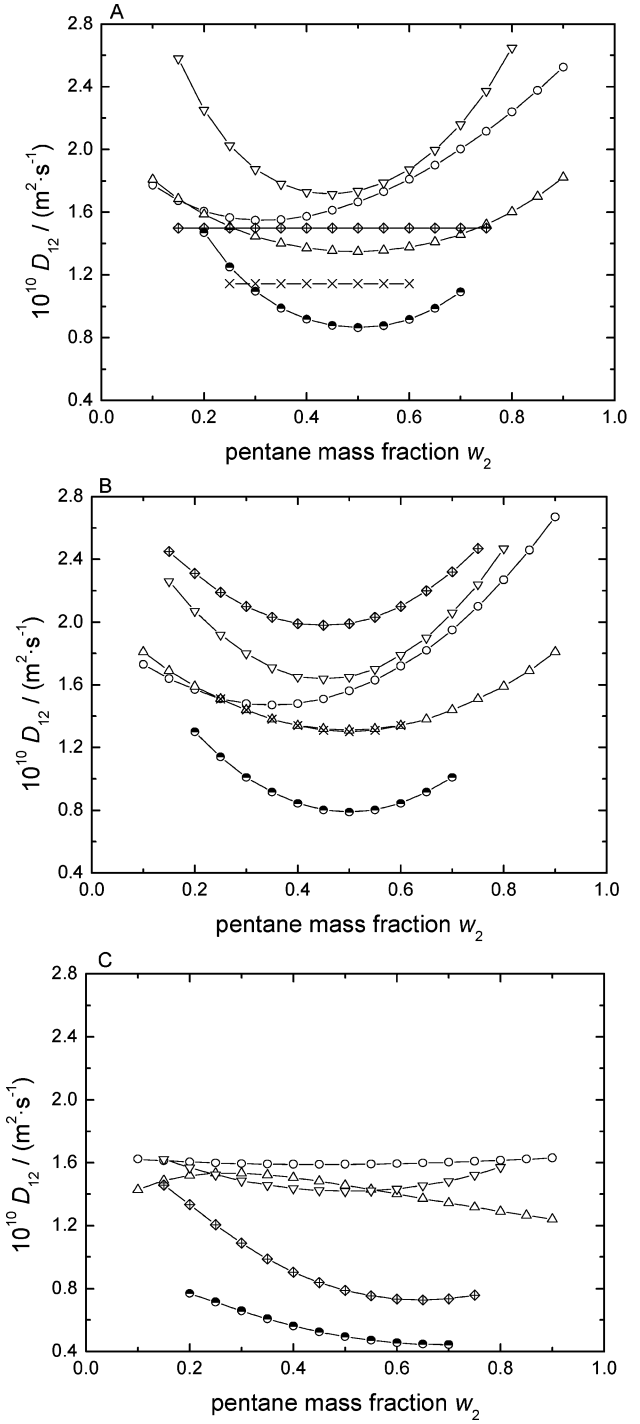

Figure 2. Computed mutual diffusion coefficients based on composition profiles for the mixture Athabasca bitumen (1) + pentane (2) at 295 K. Panel A: Equations 3 to 12 (smoothed data). Panel B: Equations 12 to 14 (smoothed data). Panel C: Equations 3 to 12 (raw data). —○—, 1800 s; —△—; 5400 s; —▽—,12600 s; —◇— 19800 s; —◓—, 37800 s; —×—, 88200 s. The data for 88200 s are not presented in Figure 2C since the composition profile was too noisy and the derivatives were too small.

Conclusions

Direct measurement of composition profiles within liquid phases along with the analysis of the composition profiles, which accounts for variation of mutual diffusion coefficient and fluid density with composition, provide a sound basis for the computation of mutual diffusion coefficient for mixtures with large density differences between components such as bitumen + pentane. Liquid-phase mutual diffusion coefficients (D_{12}) for bitumen (1) in pentane (2) at 295 K were obtained over composition range $w_2 = (0.1 \text{ to } 0.9)$. The values appear to be constant $(1.7 \pm 0.4) \cdot 10^{-10}\ \mathrm{m^2 \cdot s^{-1}}$ in this concentration interval. Extrapolation to infinite dilution of bitumen in pentane

($w_2 \rightarrow 1$) yield values significantly lower than those predicted by the Wilke−Chang equation, which assumes that the molecules are not aggregated. Planned improvements in the composition and spatial resolution of composition profiles will improve the accuracy of the mutual diffusion coefficients and extend the concentration ranges examinable. However, the improvements may not lead to better prediction of the mutual diffusion coefficients at infinite dilution because asphaltenes, a key constituent of bitumen and heavy oil, remain aggregated at low concentrations.

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