Experimentally Validated Model for the Determination of Concentration-Dependent Diffusion of a Light Hydrocarbon in Bitumen

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ABSTRACT: A simple experiment of transient, one-dimensional diffusion of pure butane vapor into bitumen was designed that permitted direct measurement of bitumen swelling and butane uptake with time. The experimental results showed significant swelling as a result of butane uptake by the viscous liquid. A mathematical model that rigorously accounts for the dependence of both density and mutual diffusion coefficient on liquid composition was developed and used to interpret the experimental data. Given the dependence of mixture density on composition, the concentration dependence of the diffusion coefficient of butane in bitumen was determined using least-squares nonlinear regression. It was found that the dependence of diffusion coefficient on concentration cannot be ascertained from butane uptake or bitumen swelling data alone. In isolation, either set of experimental data (bitumen swelling or butane uptake) can be fitted equally well with rather different functions describing the dependence of diffusion coefficient on composition. Validation against experimental data not used to fit model parameters, however, suffices for discriminating between candidate concentration-dependent diffusivities. These findings improve our ability to accurately measure the diffusivity of light n-alkanes in bitumen, information that is relevant to the understanding of in situ heavy oil recovery using hydrocarbon solvents.

1.0. INTRODUCTION

As the global demand for petroleum products grows and the rate of discovery of easily accessible hydrocarbon resources declines, increased attention is drawn to enhanced oil recovery of already produced conventional oil reserves and to the production of unconventional resources such as heavy oil and bitumen. Light hydrocarbon vapors or CO₂ can be used as solvents in the recovery of both conventional and unconventional hydrocarbon resources from subsurface formations.

Light hydrocarbons or CO₂ are injected into conventional oil reservoirs at the completion of a water drive in an attempt to displace the disconnected oil ganglia trapped within the pore space toward the production well. Reduction of the oil—water interfacial tension and swelling of the oil phase due to the dissolution of the injected solvent are believed to result in additional oil recovery during injection of light hydrocarbons or CO₂.¹ Hydrocarbon solvents are also injected for the in situ recovery of heavy oil or bitumen where the intended effect is the reduction of oil viscosity that accompanies the mixing of the oil with the injected solvent. Recovery of the diluted heavy oil or bitumen by gravity-driven flow toward a production well becomes economical.² Diffusion plays a prominent role in the transport of solvent mass into the oil phase in either recovery process.

A lack of predictive models has resulted in considerable effort being devoted to the experimental determination of the diffusivity of light hydrocarbon vapors or CO₂ gas in oil.³−¹⁵ The experiment typically involves exposing a known mass of oil to CO₂ gas or light hydrocarbon vapor and determining the amount of solute that diffuses into the oil phase as a function of time. The rate of swelling of the oil and/or the rate of decay of the overhead gas phase pressure is experimentally measured. A mathematical model of the diffusion process is always required for interpreting the experimental data. Inevitably, diffusivity estimates obtained by model fitting to data are sensitive to model assumptions, a fact which has motivated a number of additional studies.¹¹,¹⁶−¹⁹ Others have advocated the use of sophisticated instrumentation such as X-ray tomography for monitoring the diffusion process, attempting to deduce the spatiotemporal evolution of the concentration of light n-alkanes in heavy oil or bitumen from measurements of X-ray attenuation.⁴,²⁰,²¹

Our interest in the determination of the diffusivity of light hydrocarbon vapors in heavy oil or bitumen stems from what we perceive to be an inadequate account of the consequences of the significant solubility of light hydrocarbon vapors in heavy oil or bitumen. Solvent extraction processes such as VAPEX²²−²⁷ and to some extent N-Solv²⁸ rely on the diffusion of light hydrocarbons (propane or butane) into the extremely viscous (10⁵−10⁶ cP) oil phase in order to reduce the oil phase viscosity and mobilize it under the force of gravity. The live oil produced, which has a viscosity of less than 10 cP, contains solvent to an amount of 30−60 wt %. This fact has two important consequences. First, diffusion takes place in a concentrated liquid solution where the assumption of concentration-independent diffusion coefficient is generally invalid.³⁰,³¹,³² Second, very significant density reduction and swelling of the liquid mixture accompanies the diffusion process, such that the vapor—liquid interface is a moving interface and the liquid mixture cannot be considered stagnant.³³ Attempts to account for one or the other (but not both) of these consequences in the interpretation of
experimental data have been made. Studies making use of X-ray tomography to deduce the spatiotemporal evolution of diffusing species concentration in n-alkane/bitumen mixtures have indeed considered the effect of composition on both liquid density and diffusion coefficient. These studies, however, have failed to reveal the exact dependence of diffusivity on composition only illustrating that there appears to be dependence. We have not been able to find any published estimates of the diffusivity of light hydrocarbons in heavy oil or bitumen that have been validated against experimental data not used to obtain these estimates.

We report here on a straightforward method to determine the concentration-dependent diffusivity of a light hydrocarbon (n-butanone) in bitumen. The method consists of a simple experiment and a corresponding mathematical model. This method is novel because it permits independent experimental validation of the functional form of the dependence of diffusivity on concentration. The paper is structured as follows. A mathematical model of one-dimensional diffusion of a single-component vapor into a nonvolatile liquid is first developed. This model is valid for binary diffusion in concentrated, potentially nonideal, liquid mixtures undergoing significant density changes (swelling). The subsequent section, Experimental Aspects, discusses the physical realization of this model and provides details of the experimental system which permits the monitoring over time of both the rate of bitumen swelling and the rate of butane uptake by the bitumen, under conditions of constant temperature and pressure. Analysis of the experimental data involves parameter estimation using the model of the diffusion process and is presented next. It is concluded that fitting of the rate of butane uptake or the rate of bitumen swelling alone is not sufficient to uniquely determine the dependence on concentration of butane diffusivity in bitumen. Both sets of data must be considered—the first to fit the linear diffusion model and the second with which to validate the first. Contrary to recent reports, the diffusion coefficient of butane in Athabasca bitumen is shown to depend linearly on the mass fraction of butane.

2.0. MATHEMATICAL MODEL

We consider one-dimensional ordinary diffusion in a binary isothermal liquid consisting of butane (component s) and bitumen (component b) confined in the domain 0 ≤ z ≤ z_b(t), where z_b(t) is the height of the liquid column and z = z_b(t) indicates the vapor—liquid interface. Bitumen is actually a mixture of a very large number of different compounds, the molecular structure of which is not completely known. The treatment of bitumen as a single-component fluid is motivated by the need to render the diffusion problem tractable.

The continuity equation (mass balance) of component s in a fixed reference frame in Cartesian coordinates is given by

$$\frac{\partial (\rho_s)}{\partial t} + \frac{\partial}{\partial z}(\rho_s V^m) - \frac{\partial j_s}{\partial z} = 0$$  \hspace{1cm} (1)

where \(\rho_s\) and \(j_s\) are the mass concentration and diffusive mass flux of butane, respectively, and \(V^m\) is the mass average velocity of the liquid mixture. The mass flux for ordinary diffusion in a binary system, \(j_s\), is given by

$$j_s = -D^m_s \nabla \rho_s$$  \hspace{1cm} (2)

where \(c\) is the total molar concentration, \(\rho\) is the mixture density, \(M_s\) and \(M_b\) are the molar masses of butane and bitumen, respectively, \(D^m_s\) is the binary diffusion coefficient, and \(x_s\) and \(a_s\) are the mol fraction and activity of butane, respectively. The mixture density for an ideal solution, for which the excess molar volume is zero, is given by

$$\rho = \frac{1}{v^c_s a_s + v^c_b (1 - a_s)}$$  \hspace{1cm} (3)

where \(v^c_s\) and \(v^c_b\) are the specific volumes of pure butane and undiluted bitumen, respectively, and \(a_s \equiv \rho_s / \rho\) is the mass fraction of butane. Ideal solutions can be simplified using \(\partial \ln \alpha_s / \partial \ln x_s = 1\) and thus eq 2 becomes

$$j_s = -\rho D^m_s \nabla x_s$$

and eq 1 becomes

$$\frac{\partial (\rho_s)}{\partial t} + \frac{\partial}{\partial z}((\rho_s V^m) - \frac{\partial}{\partial z}(\rho D^m_s \frac{\partial \alpha_s}{\partial z})) = 0$$  \hspace{1cm} (4)

with \(\rho\) given by eq 3. The following mathematical development assumes that the bitumen—bitumen mixture is ideal, since data available for a very similar system (Athabasca bitumen–propane) show very small deviations from ideality. We emphasize, however, that the assumption of ideal solution behavior is not essential to the development and may be readily relaxed if the dependence of activity and excess molar volume on composition is known. Regardless, the binary diffusion coefficient, \(D^m_{sb}\), is expected to depend on composition. A number of equations for \(D^m_{sb}(x_s)\) can be found in the literature, although it is presently unknown if any of them apply to light hydrocarbon–bitumen mixtures. Vignes reported an empirical equation, which for ideal binary solutions reads

$$D^m_{sb} = D^m_{s_b} D^m_{b_s}$$  \hspace{1cm} (5)

where \(D^m_{s_b}\) and \(D^m_{b_s}\) are the binary diffusion coefficients in the limits of infinite dilution of bitumen and butane, respectively. A modification of the above equation by Leffler and Cullinan makes use of the component and mixture viscosities

$$D^m_{sb} = (D^m_{s_b})^{x_s} (D^m_{b_s})^{x_b}$$  \hspace{1cm} (6)

This paper also considers a linear dependence of binary diffusion coefficient on solvent mass fraction in the following form

$$D^m_{sb} = \omega_s D^m_{s_b} + (1 - \omega_s) D^m_{b_s}$$  \hspace{1cm} (7)

There are two independent mass conservation statements for a binary isothermal system: one for component s, eq 4, and one for the entire mixture, as shown below

$$\frac{\partial \rho}{\partial t} = -\rho \frac{\partial V^m}{\partial z} - V^m \frac{\partial \rho}{\partial z}$$  \hspace{1cm} (8)

Equation 4 and eq 8 are necessary and sufficient for describing the diffusion process of interest. Yet, it is clear that the mixture density, \(\rho\), and butane mass concentration, \(\omega_s\), are unwieldy dependent variables. It is preferable to cast the diffusion problem in terms of the mass fraction of butane in the bitumen, \(\omega_s = \omega_s(x_s(t))\), and the height of bitumen column, \(z_b = z_b(t)\), as the two dependent variables. Equation 4 is rewritten using \(\rho_s \equiv \omega_s \rho\) as follows
follows. Multiplication of eq 10 by \( \rho \) from a total mass balance on a control volume encompassing the cross-sectional area of the top surface of the bitumen column). The boundary conditions, then yields

\[
\frac{\partial \rho_0}{\partial t} + \rho V^m \frac{\partial \rho_0}{\partial z} - \frac{\partial}{\partial z} \left( \rho D_{b} \frac{\partial \rho_0}{\partial z} \right) = 0
\]

which can be also written as

\[
\frac{\partial \rho_0}{\partial t} = -V^m \frac{\partial \rho_0}{\partial z} + \frac{1}{\rho} \frac{\partial}{\partial z} \left( \rho D_{b} \frac{\partial \rho_0}{\partial z} \right)
\]

An expression for the mass average velocity, \( V^m \), is obtained as follows. Multiplication of eq 10 by \( \partial \rho / \partial \rho_0 \) leads to

\[
\rho \frac{\partial \rho_0}{\partial t} + \rho V^m \frac{\partial \rho_0}{\partial z} - \frac{\partial}{\partial z} \left( \rho D_{b} \frac{\partial \rho_0}{\partial z} \right) = 0
\]

Combining eq 12 and eq 8 and rearranging yields

\[
\frac{\partial V^m}{\partial z} = -\frac{1}{\rho^2} \frac{\partial \rho}{\partial \rho_0} \left[ \frac{\partial}{\partial z} \left( \rho D_{b} \frac{\partial \rho_0}{\partial z} \right) \right]
\]

which may be integrated\(^\text{37}\) to obtain

\[
V^m(z, t) = -\int_0^z \frac{1}{\rho^2} \frac{\partial \rho}{\partial \rho_0} \left[ \frac{\partial}{\partial z} \left( \rho D_{b} \frac{\partial \rho_0}{\partial z} \right) \right] dz
\]

Equation 14 is simplified by making use of eq 3 to yield

\[
V^m(z, t) = (v^*_b - v^*_s) \int_0^z \left[ \frac{\partial}{\partial z} \left( \rho D_{b} \frac{\partial \rho_0}{\partial z} \right) \right] dz
\]

The mass average velocity, \( V^m \), as shown by eq 15, originates from the diffusive mixing of two components with different specific volumes and would be zero if \( v^*_b = v^*_s \). If \( V^m \) from eq 15 is substituted into eq 11, one obtains a statement of butane conservation in terms of the butane mass fraction in the liquid phase. Integration of eq 11, subject to appropriate initial and boundary conditions, then yields \( \omega_s(z, t) \) in \( 0 \leq z \leq z_b(t) \).

We obtain the differential equation for the evolution of the height of the bitumen column with time, \( z_b = z_b(t) \), by starting from a total mass balance on a control volume encompassing the liquid phase

\[
\frac{d}{dt} \left[ A_b \int_0^{z_b(t)} \rho(z, t) dz \right] = A_b \left( \rho D_{b} \frac{\partial \rho_0}{\partial z} \right)_{z=z_b(t)}
\]

The left-hand side of eq 16 represents the rate of increase of mass within the control volume, whereas the right-hand side represents the rate of mass influx by diffusion into the control volume through a control surface of cross-sectional area \( A_b \) (the cross-sectional area of the top surface of the bitumen column). The Leibniz rule is used to rewrite eq 16 as follows

\[
\int_0^{z_b(t)} \frac{\partial \rho}{\partial t} dz + \rho(z_b(t)) \frac{\partial z_b}{\partial t} \bigg|_{t=z_b} = \left( \rho D_{b} \frac{\partial \rho_0}{\partial z} \right)_{z=z_b(t)}
\]

or, equivalently,

\[
\frac{dz_b}{dt} = \left( \frac{D_{b}}{\rho} \frac{\partial \rho_0}{\partial z} \right)_{z=z_b(t)} - \frac{1}{\rho(z_b(t))} \int_0^{z_b(t)} \frac{\partial \rho}{\partial t} dz
\]

An alternative form of eq 18, which does not contain the time-derivative of the density, facilitates the numerical solution. This may be obtained with the help of eq 3 and reads as follows

\[
\frac{dz_b}{dt} = \left( \frac{D_{b}}{\rho} \frac{\partial \rho_0}{\partial z} \right)_{z=z_b(t)} - \frac{1}{\rho(z_b(t))} \int_0^{z_b(t)} \frac{\partial \rho}{\partial t} dz
\]

A complete statement of the diffusion problem thus consists of eqs 11, 15, and 19, augmented with the following initial and boundary conditions

\[
\begin{align*}
\omega_s(z, 0) &= 0; & 0 \leq z \leq z_b(t) \\
\omega_s(z_b(t), t) &= \omega^*_b; & t > 0 \\
\frac{\partial \rho_0}{\partial z} \bigg|_{z=0} &= 0; & t > 0
\end{align*}
\]

where \( z_b(t) \) is the initial height of the bitumen column and \( \omega^*_b \) is a constant equal to the solubility of butane in bitumen at the prevailing constant temperature and pressure. The physical realization of the mathematical model stated above is described in the next section. It is important to observe that the model predicts an evolution of the height of the bitumen column with time, \( z_b = z_b(t) \), that is independent of the cross-sectional area \( A_b \) available for mass transfer. We shall take advantage of this observation to test experimentally the assumption of one-dimensional diffusion in a subsequent section.

As stated, the problem is complicated by the presence of a moving boundary at \( z = z_b(t) \). This complication may be easily overcome by employing the so-called "front-fixing" approach, first proposed by Landau\(^\text{38}\) and described by Crank.\(^\text{39}\) Accordingly, a dimensionless space coordinate, \( \xi = z/z_b(t) \), is defined such that the diffusion domain is now confined in \( 0 \leq \xi \leq 1 \). The requisite transformations of eqs 11, 15, and 19 are accomplished with the help of the following formulas

\[
\frac{\partial \omega_s}{\partial \xi} = \frac{1}{z_b(t)} \frac{\partial \omega_s}{\partial \xi}
\]

\[
\frac{\partial^2 \omega_s}{\partial \xi^2} = \frac{1}{z_b(t)^2} \frac{\partial^2 \omega_s}{\partial \xi^2}
\]

\[
\frac{\partial \rho_0}{\partial \xi} = -\frac{\xi}{z_b(t)} \frac{\partial \rho_0}{\partial t} + \frac{\partial \rho_0}{\partial t}
\]

Using the above expressions, we obtain for the mass balance of butane

\[
\frac{\partial \rho_0}{\partial \xi} = \left( \frac{\xi}{z_b(t)} \frac{\partial \rho_0}{\partial \xi} + \frac{\partial \rho_0}{\partial \xi} \right) \left[ \frac{D_{b}}{\rho z_b(t)^2} \frac{\partial \rho}{\partial \xi} \right] + \frac{1}{z_b(t)} \frac{\partial D_{b}}{\partial \xi} - V^m \left( \frac{\partial \rho}{\partial \xi} \right)_{z_b(t)^2} \frac{\partial \rho}{\partial \xi}
\]

where
Equation 19 is also transformed to

$$\frac{dz_b}{dt} = \frac{D_{lb}}{z_b(t)} \frac{\partial \alpha_l}{\partial \xi} \bigg|_{\xi=0} - \frac{(v^b_0 - v^b)}{\rho(z_b, t)} \int_0^1 \rho^2 \left[ \frac{\xi}{z_b(t)} \frac{dz_b}{dt} \frac{\partial \alpha_l}{\partial \xi} + \frac{\partial \alpha_l}{\partial t} \right] z_b(t) \, d\xi$$

(24)

Note that eq 24 is implicit in $dz_b/dt$. The initial and boundary conditions are restated as

$$z_b(0) = z_{b,0}, \quad 0 \leq \xi \leq 1$$

(25a)

$$\alpha_l(\xi, 0) = 0; \quad t > 0$$

(25b)

$$\alpha_l(1, t) = 0; \quad \xi = 0; \quad t > 0$$

(25c)

(25d)

The system of equations, eqs 22−25, is ideally suited for numerical integration using the method of lines—a task detailed in the Appendix.

3.0. EXPERIMENTAL ASPECTS

3.1. Apparatus and Procedure. The experimental apparatus, depicted schematically in Figure 1, consists of two interconnected glass reservoirs kept in separate constant-temperature water baths. The first reservoir, which acts as the source of light hydrocarbon vapor, is a 1/4 in. glass capillary (total length = 40 cm, vertical length = 30 cm) with an inner diameter (ID) of 0.3915 cm. This reservoir contains liquid n-butane. The second reservoir is a 10-cm long glass tube (OD = 15 mm, ID = 9.92 or 11.18 mm) with a flat bottom at $z = 0$. This reservoir, hereafter referred to as the diffusion cell, contains the bitumen. Stainless steel fittings (Swagelok) and nylon ferrules were used to connect the glass tubing. Nonlubricated valves (Swagelok) are used at the top of both the butane container (1/4 in. two-way valve) and the diffusion cell (1/4 in. two-way valve). A reducing union and reducing port $T_b$, connector are used to connect the 15-mm glass tube to the 1/4 in. three-way valve. Face seals are used to seal the 1/4 in. stainless steel tubing running through the walls of each of the water baths. Temperature controllers are used to maintain the temperature of the two water baths independently. The temperature of the butane, $T_{b,0}$ is maintained 1−2 °C lower the temperature of the bitumen, in order to prevent butane vapor from condensing in the diffusion cell. Vibration of the diffusion cell is eliminated by isolating the temperature controllers and mixers from the water baths and by placing the water baths on a vibration-free table. Temperatures are monitored at 30 s time intervals using type-T thermocouples (Omega) connected to an 8-channel data acquisition board (Measurement Computing USB-TC) and recorded using LabVIEW software (National Instruments). Subsequent to purging of air from the system (see below), diffusion of butane into bitumen takes place at constant temperature, $T_{b}$, and constant pressure equal to the vapor pressure of butane, $P_v(T_{b})$. The decrease of the level of liquid butane in the glass capillary with time, $\Delta h_b(t) = h_b(0) - h_b(t)$, and the increase of the height of bitumen in the diffusion cell with time, $\Delta z_b(t) = z_b(t) - z_b(0)$, are both observed directly using a cathetometer and recorded during this process. Uncertainty in the measurements of $h_b$ and $z_b$ is due to the precision of the cathetometer readings (±0.01 mm), as well as the inaccuracy of visually locating the liquid−vapor interface. The total mass of butane transferred into the bitumen at any time during the diffusion process is readily found using the experimentally measured, $\Delta h_b(t)$, as

$$m_{\text{trans}}(t) = \rho_b^{(l)} A_b \Delta h_b(t)$$

(26)

where $\rho_b^{(l)}$ is the density of liquid butane at temperature equal to $T_{b}$, and $A_b$ is the cross-sectional area of the glass capillary containing liquid bitumen. It is important to note that $m_{\text{trans}}(t)$ is predicted by the mathematical model as

$$m_{\text{trans}}(t) = A_b \int_0^{\Delta z_b(t)} \rho_{\text{vap}} \, dz$$

(27)

Charging the diffusion cell with bitumen must be performed carefully to avoid smearing it on the tube wall. This was done as follows. A pressure vessel containing the highly viscous bitumen was connected via a metering valve to a needle constructed of 1/8 in. stainless steel tubing. This system was placed on a heat and heated inside a convection oven to reduce the bitumen viscosity. The vessel was pressurized to 30 psig (206.84 kPa) with air, the needle inserted into the diffusion cell, and the valve opened to allow the bitumen to fill the diffusion cell. A number of diffusion cells were filled to approximately the same level. These cells were then weighed, and two with equal mass were chosen for replicate testing. The butane capillary tubes were filled by placing them in ice and connecting them to a supply of butane, subsequent to purging of air from the supply line. The butane readily condensed in the cold capillary tubes.

Once the filled bitumen and butane tubes were connected and the constant-temperature baths filled with water, the entire system was equilibrated for several hours prior to purging the system of air. The purge sequence was as follows. First, the vent side of the three-way valve on the diffusion cell was connected to vacuum. The butane valve was then opened. Butane vapor was admitted to the diffusion cell for five seconds by using the three-way valve to connect the diffusion cell to the butane reservoir. Subsequently, the diffusion cell was connected to vacuum for 5 s. The vapor fill−vacuum purge sequence was repeated five times. Butane vapor was admitted to the diffusion cell for a sixth time, except that this time the diffusion cell now contained butane vapor at atmospheric pressure and the diffusion cell was disconnected from the liquid butane reservoir. The levels of liquid butane, $h_b(0)$, and bitumen, $z_b(0)$, in the respective reservoirs were immediately recorded and the experiment was initiated by using the three-way valve to connect the diffusion cell to the bitumen reservoir. Replicate experiments were carried out concurrently, so as to correspond to identical temperature and pressure conditions.
3.2. Fluid Properties. Key physical properties of butane and Athabasca bitumen at experimentally relevant conditions are listed in Table 1. The bitumen was kept in a convection oven at 373.5 K for several days prior to any testing. This was done to ensure compliance with one of the model assumptions, namely that the bitumen can be considered a nonvolatile liquid. The bitumen was analyzed by Maxxam Analytics Inc. with results shown in Table 2. The tabulated data include the average molar mass, $M_b$ (ASTM D2503), the bitumen density, $\rho_b$ (ASTM D4052), as well as the boiling point determined from simulated distillation (ASTM D5307), API gravity (ASTM D4052), and sulfur content (ASTM 4294) of different fractions. Additional information includes measurements of the viscosity of different bitumen fractions at three different temperatures (ASTM D445). The assay results were used to estimate the solubility, $\omega_T$, of butane in the Athabasca bitumen by means of an equilibrium flash calculation carried out in Aspen Plus (version 2006) using the Peng–Robinson equation of state. The point identified the solubility of butane at the experimental conditions.

The viscosity of undiluted bitumen was also determined experimentally at different temperatures, and the results fitted ($R^2 = 0.9958$) to the following empirical equation

$$\mu_b = 1.74 \times 10^9 e \cdot 0.5175 + 3.05 \times 10^7 e \cdot 0.18447$$

with $T$ in deg celsius and $\mu_b$ in centipoise. The viscosity, $\mu_{mix}$, of bitumen–butane mixtures was estimated using the following correlation proposed by Shu$^{40}$

$$\ln \mu_{mix} = \left( \frac{\alpha V_b}{\alpha V_b + V_s} \right) \ln \mu_b + \left( 1 - \frac{\alpha V_b}{\alpha V_b + V_s} \right) \ln \mu_s$$

in which $V_s$ and $V_b$ are the volumes of bitumen and butane in the mixture and $\alpha$ is an empirical constant taking values between zero and unity. The constant $\alpha$ was computed from Shu$^{40}$ as

$$\alpha = 17.04(SG_b - SG_s)^{0.5237}SG_b^{3.2745}SG_s^{1.6316}$$

where $SG_b$ and $SG_s$ are the specific gravity of bitumen and butane at the prevailing conditions of temperature and pressure. Note that the viscosity, $\mu_{mix}$, of bitumen–butane mixtures is only required for the estimation of the diffusion coefficient, $D_{mix}$, using the Leffler and Cullinan$^{43}$ correlation, eq 6.

3.3. Diffusion Experiments. A preliminary experiment, aimed at testing the adequacy of the assumption of 1D diffusion, was carried out first. The two diffusion cells used in that experiment were of different

![Figure 2. Estimated solubility of n-butane in Athabasca bitumen using the Peng–Robinson equation of state. The point identifies the solubility of butane at the experimental conditions.](image-url)

### Table 1. Basic Properties of Fluids used in Diffusion Experiments

<table>
<thead>
<tr>
<th>measurement/property</th>
<th>solvent (s)</th>
<th>bitumen (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>type</td>
<td>n-butane</td>
<td>Athabasca</td>
</tr>
<tr>
<td>molecular mass (g·mol$^{-1}$)</td>
<td>58.12</td>
<td>557</td>
</tr>
<tr>
<td>liquid density (g·cm$^{-3}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 24.9 °C</td>
<td>0.57295$^a$</td>
<td></td>
</tr>
<tr>
<td>at 26.3 °C</td>
<td>0.57132$^a$</td>
<td></td>
</tr>
<tr>
<td>at 22 °C</td>
<td>0.15645$^a$</td>
<td>238441</td>
</tr>
<tr>
<td>viscosity at 26.3 °C (cP)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$From Llemmon et al. (2008).$^{43}$

### Table 2. Bitumen Properties Relevant to Thermodynamic Modeling by ASPEN-Plus

<table>
<thead>
<tr>
<th>percent distilled</th>
<th>temp (°C)</th>
<th>mid % distilled</th>
<th>API gravity</th>
<th>sulfur content</th>
<th>kinematic viscosity (m$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15.5 °C</td>
<td>50 °C</td>
<td>100 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>194.5</td>
<td>0</td>
<td>8.3</td>
<td>4.969</td>
<td>5.491 × 10$^{-6}$</td>
</tr>
<tr>
<td>5</td>
<td>264.8</td>
<td>2.27</td>
<td>29.5</td>
<td>1.454</td>
<td>1.35 × 10$^{-5}$</td>
</tr>
<tr>
<td>10</td>
<td>305.1</td>
<td>6.22</td>
<td>24.85</td>
<td>1.728</td>
<td>1.331 × 10$^{-4}$</td>
</tr>
<tr>
<td>15</td>
<td>335.1</td>
<td>9.12</td>
<td>17.97</td>
<td>2.338</td>
<td>1.25 × 10$^{-3}$</td>
</tr>
<tr>
<td>20</td>
<td>362.0</td>
<td>16.64</td>
<td>14.35</td>
<td>3.584</td>
<td>8.09 × 10$^{-3}$</td>
</tr>
<tr>
<td>25</td>
<td>397.7</td>
<td>35.06</td>
<td>12.08</td>
<td>3.853</td>
<td>7.042 × 10$^{-3}$</td>
</tr>
<tr>
<td>30</td>
<td>412.8</td>
<td>56.22</td>
<td>6.07</td>
<td>5.197</td>
<td>4.335 × 10$^{-3}$</td>
</tr>
<tr>
<td>40</td>
<td>458.4</td>
<td>70.07</td>
<td>1.66</td>
<td>6.344</td>
<td>4.989 × 10$^{-2}$</td>
</tr>
<tr>
<td>50</td>
<td>508.1</td>
<td></td>
<td></td>
<td></td>
<td>5.197 × 10$^{-4}$</td>
</tr>
<tr>
<td>60</td>
<td>564.1</td>
<td></td>
<td></td>
<td></td>
<td>5.396 × 10$^{-2}$</td>
</tr>
<tr>
<td>70</td>
<td>623.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>677.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>718.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
diameters (9.92 ± 0.02 and 11.18 ± 0.08 mm), as it was expected that deviation from the assumption of 1D diffusion would manifest itself as a dependence of \( \Delta z_b(t) \) on the cross-sectional area, \( A_{sb} \), of the diffusion cell. Experimental data from this test, shown in Figure 3, reveal no significant effect of the difference in cross-sectional area, \( A_{sb} \), on \( \Delta z_b(t) \) over 4800 min of butane diffusion into bitumen. Furthermore, the total mass of butane transferred into the bitumen, which is directly proportional to the decrease of the level of liquid butane in the glass capillary, \( \Delta h_b(t) \), is also proportional the cross-sectional area, \( A_{sb} \), of the vapor–liquid interface through which diffusion takes place. The results shown in Figure 3 verify the theoretical expectation that \( \Delta h_b(t) = \Delta z_b(t) \) be equal to \( \Delta l_{sb}^{(1)}/A_{sb}^{(1)} \) = 1.26, lending further support to the assumption of 1D diffusion. Two separate diffusion tests were subsequently carried out, each test involving two diffusion cells connected to respective butane reservoirs. As shown in Table 3, the experiments were conducted at the same \( T_s \) and \( T_b \) conditions, the only difference between them being the amount of bitumen used to fill the pair of diffusion cells used in each diffusion test.

4.0. RESULTS AND DISCUSSION

Experimental measurements of \( \Delta z_b(t) \) and \( \Delta h_b(t) \) are summarized in Figure 4 for all diffusion experiments in Table 2. Both \( \Delta z_b(t) \) and \( \Delta h_b(t) \) are shown to increase linearly with the square root of time, as expected for a diffusion-dominated process. Results from replicate experiments are not statistically different and, for ease of comparison with model predictions, were regressed together to give \( \Delta z_b(t) = 0.0244 \sqrt{t} \) and \( \Delta h_b(t) = 0.1602 \sqrt{t} \), where time is in seconds and \( \Delta z_b(t) \) and \( \Delta h_b(t) \) are in millimeters.

The mathematical model of 1D diffusion of butane into bitumen predicts the increase in the level of liquid phase, \( \Delta z_b(t) \), provided that the functional dependence of binary diffusion coefficient on composition, \( D_{sb}(x) \), is specified. Each of eqs 5, 6, and 7 is a two-parameter model of the functional dependence of binary diffusion on composition. Experimental measurements and model predictions of \( \Delta z_b(t) \) were used to estimate best-fit values of the parameters \( D_{sb}^c \) and \( D_{sb}^0 \) for each diffusivity model plus a constant diffusion coefficient being a best-fit parameter itself. Specifically, the following objective function

\[
F_{obs}(D_{sb}^c, D_{sb}^0) = \sum_{i=1}^{N} \frac{\left( \Delta z_b^{(exp)}(t_i) - \Delta z_b^{(mod)}(t_i) \right)^2}{\Delta z_b^{(exp)}(t_i)}
\]  

was minimized using a nonlinear least-squares routine in Matlab. It should be distinctly noted that only the bitumen data was fitted. Best-fit values of the parameters are summarized in Table 4 for two values of \( \omega_s^\alpha \) and corresponding model predictions of \( \Delta z_b(t) \) are compared to experimental data in Figure 5. It is evident that an equally good fit of the experimental data on bitumen swelling is achieved for every type of concentration dependence and for both values of \( \omega_s^\alpha \) after appropriate adjustment/fitting of the parameters \( D_{sb}^c \) and \( D_{sb}^0 \). Clearly, the functional dependence of binary diffusion coefficient on composition cannot be uniquely determined by considering bitumen swelling data alone. This is emphasized in Figure 6, which plots the Vignes31 model eq 5, the Leffler and Cullinan6 model eq 6, and the linear model eq 7 with \( D_{sb}^c \) and \( D_{sb}^0 \) values from Table 4, in addition to constant diffusivity. Figure 7 illustrates the distinctively different liquid density

![Figure 3. One-dimensional diffusion is consistent with an increase in bitumen level (mm) independent of cross section: (■) ID = 11.15 mm and (●) ID = 9.95 mm. The decrease in butane level (mm) increases with increasing mass transfer area: (○) ID = 11.15 mm and (□) ID = 9.95 mm.](image)

![Figure 4. The change in height is square root dependent with time for both the increase in bitumen level (●) where \( y = 0.0244x \) with an \( R^2 = 0.9947 \) and the decrease in butane level (○) where \( y = 0.1602x \) with an \( R^2 = 0.9943 \).](image)

Table 3. Experimental Conditions

<table>
<thead>
<tr>
<th>measurement/property</th>
<th>experiment 1</th>
<th>experiment 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>average butane temperature, ( T_s ) (°C)</td>
<td>24.9</td>
<td>24.9</td>
</tr>
<tr>
<td>average bitumen temperature, ( T_b ) (°C)</td>
<td>26.3</td>
<td>26.3</td>
</tr>
<tr>
<td>mass of bitumen (g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sample 1</td>
<td>1.33126</td>
<td>1.58222</td>
</tr>
<tr>
<td>sample 2</td>
<td>1.33076</td>
<td>1.58475</td>
</tr>
<tr>
<td>average</td>
<td>1.33101 ± 0.00025</td>
<td>1.58349 ± 0.00127</td>
</tr>
</tbody>
</table>

Table 4. Best-Fit Values of the Parameters of Different Models of Concentration-Dependent Diffusion Coefficient for \( \omega_s^\alpha = 0.60 \) and 0.45

<table>
<thead>
<tr>
<th>model</th>
<th>( D_{sb}^c ) (cm²·s⁻¹)</th>
<th>( D_{sb}^0 ) (cm²·s⁻¹)</th>
<th>( D_{sb}^c ) (cm²·s⁻¹)</th>
<th>( D_{sb}^0 ) (cm²·s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vignes, eq 5</td>
<td>8.66 × 10⁻⁶</td>
<td>7.54 × 10⁻⁶</td>
<td>13.0 × 10⁻⁶</td>
<td>7.55 × 10⁻⁶</td>
</tr>
<tr>
<td>Leffler and Cullinan, eq 6</td>
<td>9.04 × 10⁻⁷</td>
<td>9.05 × 10⁻⁷</td>
<td>27.1 × 10⁻⁶</td>
<td>17.5 × 10⁻⁶</td>
</tr>
<tr>
<td>linear, eq 7</td>
<td>9.69 × 10⁻⁶</td>
<td>4.91 × 10⁻⁶</td>
<td>17.6 × 10⁻⁶</td>
<td>7.48 × 10⁻⁶</td>
</tr>
<tr>
<td>constant</td>
<td>4.35 × 10⁻⁶</td>
<td>12.3 × 10⁻⁶</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
profiles corresponding to each of the functions plotted in Figure 6, despite the fact that each function produces the same rate of macroscopically observable swelling of the bitumen (see Figure 5).

As noted previously, the cumulative mass of butane transferred into the bitumen at any time during the diffusion process may be readily computed using eq 27 from model predictions of the instantaneous distribution of the butane mass fraction, $\omega_s$. Using eq 26, it is then possible to predict the corresponding decrease in the level of liquid butane, $\Delta h_b(t)$.

The latter is compared to experimental measurements in Figure 8, revealing that a linear dependence of binary diffusion coefficient on butane mass fraction, viz. eq 7, is most consistent with the experimental results. It is clearly evident that the other diffusion functions tried, namely the Vignes$^{31}$ and Leffler and Cullinan$^{36}$ models as well as a constant diffusion coefficient are not able to independently match the butane mass balance (decrease in solvent level). We found that values of $\omega_s^*$ in the range 0.45 to 0.60 result in similarly good fits of both bitumen
swelling and solvent height decrease data using the linear diffusivity model, but values of $\omega_0^i$ outside this range do not.

It is instructive to check whether the diffusion coefficient at infinite dilution of bitumen, $D_{bs}^c$, might be predicted from the Stokes–Einstein equation, which is appropriate for large spherical solutes diffusing into low-molecular weight solvents: \(^{30}\)

$$D_{bs}^c = \frac{k_BT}{6\pi \mu R_b} \quad (32)$$

where $k_B$ is the Boltzmann constant, $\mu$ is the butane solvent viscosity, and $R_b$ is an equivalent radius of bitumen molecules, roughly estimated from the molar volume, $V_b = (V_b/\ N_A)^{1/3}$ Using data from Table 1, one estimates $D_{bs}^c = 1.44 \times 10^{-5}$ cm$^2$/s, in reasonable agreement with $D_{bs}^c$ reported in Table 4 for the linear diffusivity models when $0.45 \leq \omega_0^i \leq 0.60$.

Asphaltenes settling by gravity could either redissolve or remain as a solid phase. The possible settling of asphaltenes could in principle induce convective mixing. Neither of these processes is accounted for in the diffusion model presented here.

When the VAPEX process is used to produce bitumen from porous media, transport of light hydrocarbon solvent into the bitumen causes the formation of a thin mixing zone at the macroscopic boundary between vapor- and bitumen-filled pore space. \(^{26}\) The thickness of this mixing zone is believed to be on the order of a few millimeters or just a few pore lengths \(^{3,41}\) containing bitumen of significantly lower viscosity draining under the action of gravity. \(^{7}\) Clearly, the thickness of this zone is the outcome of delicate coupling between mass transport and fluid flow, but a fundamental theoretical description is still lacking. Prediction of the rates of production of diluted bitumen during VAPEX in porous media depends on prior knowledge of the thickness of this mixing zone and of the properties (density and viscosity) of the diluted bitumen therein. \(^{41,42}\) The present work contributes to this goal by improving the description of light hydrocarbon vapor diffusion in bitumen.

5.0. CONCLUSIONS

A simple experiment was developed to monitor the rates of light hydrocarbon uptake and bitumen swelling during one-dimensional diffusion of the hydrocarbon vapor in the bitumen. Reproducible experimental data of n-butane uptake by and swelling of Athabasca bitumen at 26.3 °C were obtained. A mathematical model which accounts for the dependence of both density and diffusion coefficient on liquid composition was also developed. Assuming ideal mixing of butane with bitumen, the model was used to estimate the parameters of three empirical models of concentration-dependent diffusivity by nonlinear regression against experimental data of bitumen swelling. Model predictions of butane uptake with time agreed with experimental observations only when the dependence of diffusion coefficient was expressed as a linear function of butane mass fraction, despite the fact that experimental data of bitumen swelling could be fitted equally well by all three diffusivity models (including a model of constant diffusion coefficient). It is concluded that the dependence of diffusion coefficient on concentration cannot be discerned except with the help of a model that explicitly couples swelling of the diffusion domain with the diffusion process.

\section*{APPENDIX}

The method of lines is used to approximate the set of partial differential equations, eqs 22 and 24 by a set of ordinary differential equations for the time evolution of the height of liquid column $z_b$ and mass fraction $\omega_0^i$ at a number of discrete locations $\xi = (i - 1) \Delta \xi$ in the domain $0 \leq \xi \leq 1$, where $i = 1, 2, ..., N + 1$ and $\Delta \xi = 1/N$. Of $\xi$, accurate finite differences are used consistently to replace spatial derivatives in eqs 22 and 24 in the boundary conditions, where necessary.

\textbf{Solvent Continuity Equation 22}

Implementation of the method of lines gives $N + 1$ ordinary differential equations for $N + 1$ unknown $\omega_0^i$ as follows. For each internal node (at $i = 2, 3, ..., N$):

$$\frac{d\omega_0^i}{dt} = \left[ \frac{(i - 1) \Delta \xi}{z_b} \right] \left[ \frac{\omega_0^{i+1} - \omega_0^{i-1}}{2 \Delta \xi} \right] \frac{d\omega_0^i}{d\xi} \quad (32a)$$

$$+ \frac{1}{\Delta \xi} \left[ \frac{\omega_0^{i+1} - \omega_0^{i-1}}{2 \Delta \xi} \right] \left[ \frac{D_{bs}^{i+1} \rho^i - D_{bs}^{i-1} \rho_i}{2 \Delta \xi} \right]$$

$$+ \frac{1}{\Delta \xi} \left[ \frac{D_{bs}^{i+1} \rho^{i+1} + D_{bs}^{i-1} \rho_i}{2 \Delta \xi} \right] - V \omega_0^i (\xi) \right]$$

$$\left[ \frac{D_{bs}^{i+1} \rho^{i+1} + 2 \omega_0^i + \omega_0^{i-1}}{(\Delta \xi)^2} \right]$$

where $D_{bs}^i$ is the diffusion coefficient calculated from any one of eqs 5, 6, or 7 for a butane fraction equal to $\omega_0^i$.

The differential equation at the no-flux boundary ($i = 1$) is

$$\frac{d\omega_0^1}{dt} = \left[ \frac{2 \Delta \xi}{z_b^2} \right] \left[ \frac{\omega_0^{i+1} - \omega_0^i}{(\Delta \xi)^2} \right] \quad (32b)$$

whereas at the liquid–gas interface ($i = N + 1$)

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Figure_9.png}
\caption{Concentration profile for the numerical model results for the linear diffusivity with solubility = 0.6 mass fraction; 60 (black - - -), 300 (grey - - -), 600 (black --- ---), 1200 (grey --- ---), 1800 (black --- ---), 2400 (grey --- ---), 3600 (black ---), and 4500 (grey ---) min.}
\end{figure}
\[
\frac{d\omega_i}{dt} \bigg|_{n+1} = 0 \quad (32c)
\]

The initial conditions for the above system of ordinary differential equations is \(\omega_i^0 = 0\) for \(i = 1, \ldots, N\) and \(\omega_N^{N+1} = \omega_N^s\), where \(\omega_N^s\) denotes the solubility of butane in bitumen at the prevailing conditions of temperature and pressure.

**Mass Average Velocity, Equation 23**

The mass average velocity \(V^m\) is evaluated numerically using the multiple trapezoidal rule to approximate the integral in eq 23:

\[
V^m \equiv (v_i^m - v_i^s) \left[ \frac{(i-1)\Delta \xi}{2(i-1)} \right] f(a) + f(b) + \sum_{i=1}^{N} f(\xi_i)
\]

\[
f(a) = f(0) = 0 \quad (33a)
\]

\[
f(\xi_i) = \left( \frac{D_i^b}{z_b} \right) \left( \frac{\rho_i^{N+1} - \rho_i^{-1}}{2\Delta \xi} \right) \left( \frac{\omega_i^{N+1} - \omega_i^{-1}}{2\Delta \xi} \right) + \left( \frac{\rho_i^b D_i^b}{z_b} \right) \left( \frac{\omega_i^{N+1} - 2\omega_i + \omega_i^{-1}}{(\Delta \xi)^2} \right) \quad (33b)
\]

\[
f(\xi) = \left[ \rho(\omega_i^f) \right]^2 \left[ -\frac{(i-1)\Delta \xi}{z_b} \left( \frac{\omega_i^{N+1} - \omega_i^{-1}}{2\Delta \xi} \right) + \left( \frac{\rho_i^f}{\rho_i^b} \right) \frac{d\omega_i^f}{dt} \right] \quad (33c)
\]

**Height of Liquid Column, Equation 24**

The integral in the differential equation for the evolution of liquid height with time, eq 24, is also evaluated using the multiple trapezoidal rule. Using finite differences for the approximation of the partial derivatives, eq 24 is thus written as follows:

\[
\frac{dz_b}{dt} = \left( \frac{D_b^b(\omega_i^{N+1})}{z_b} - \frac{D_b^b(\omega_i^s)}{z_b} \right) \left( \frac{3\omega_i^{N+1} - 4\omega_i^N + \omega_i^{-1}}{2\Delta \xi} \right) + \left( \frac{\omega_i^{N+1}}{z_b} \right) \left( \frac{3\omega_i^{N+1} - 4\omega_i^N + \omega_i^{-1}}{2\Delta \xi} \right) + \left( \frac{\omega_i^{N+1} + D_b^b}{z_b} \right) \left( \frac{3\omega_i^{N+1} - 4\omega_i^N + \omega_i^{-1}}{2\Delta \xi} \right) + \left( \frac{\omega_i^{N+1}}{z_b} \right) \left( \frac{3\omega_i^{N+1} - 4\omega_i^N + \omega_i^{-1}}{2\Delta \xi} \right) \quad (34c)
\]

\[
\mathcal{F} = \left( \frac{1}{2N} \right) \left( f(a) + f(b) \right) + \frac{1}{N} \sum_{i=2}^{N} f(\xi_i) \quad (36)
\]

\[
f(a) = f(0) = \left[ \rho(\omega_i^f) \right]^2 \left( \frac{d\omega_i^f}{dt} \right) \quad (37a)
\]

\[
f(b) = f(1) = \left[ \rho(\omega_i^{N+1}) \right]^2 \left[ -\frac{(i-1)\Delta \xi}{z_b} \left( \frac{\omega_i^{N+1} - \omega_i^{-1}}{2\Delta \xi} \right) + \left( \frac{\rho_i^f}{\rho_i^b} \right) \frac{d\omega_i^f}{dt} \right] \quad (37b)
\]

\[
f(\xi) = \left[ \rho(\omega_i^f) \right]^2 \left[ -\frac{(i-1)\Delta \xi}{z_b} \left( \frac{\omega_i^{N+1} - \omega_i^{-1}}{2\Delta \xi} \right) + \left( \frac{\rho_i^f}{\rho_i^b} \right) \frac{d\omega_i^f}{dt} \right] \quad (37c)
\]

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**Notes**

The authors declare no competing financial interest.

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