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A new method for experimental measurement of diffusion coefficients in reservoir fluids

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Abstract

A simple method is presented for determining diffusion coefficients of dense gases in liquids using a PVT cell. When a non-equilibrium gas is brought into contact with a liquid in a sealed container at a constant temperature, the final state is determined by thermodynamic equilibrium. However, the time which is required to reach the final state is determined from the diffusion process in each phase. At the gas–liquid interface, thermodynamic equilibrium exists between the two phases at all times, but the position of the interface as well as the pressure may change with time.

The rate of change of pressure and the interface position as a function of time depends on the rate of diffusion in each phase and therefore on the diffusion coefficients. No compositional measurements are necessary for this method of measuring diffusion coefficients; hence, it is less expensive than conventional methods. Results obtained by this method for the binary system of methane and *n*-pentane at 311 K and 70 bar yielded diffusion coefficients within $\pm 5\%$ of literature values. The technique can be easily applied to multicomponent systems for measurement of effective diffusion coefficients in reservoir fluids.

1. Introduction

One of the most important properties in the calculation of mass transfer rates is diffusion coefficient. In petroleum reservoirs, estimation of the rate of mass transfer caused by molecular diffusion is necessary for determining the amount of gas diffusing into oil in gas injection projects (Riazi et al., 1994). In vertical miscible floods, the effect of molecular diffusion on the total amount and rate of gas dissolution is very important. Sigmund (1976), Grogan and Pinczewski (1987), Renner (1988) and Grogan et al. (1988) have discussed the importance of molecular diffusion in the study of petroleum recovery techniques. Perkins and Johnston (1963) discussed the conditions at which the diffusion process is important in comparison to dispersion in porous media. In the calculation of the rate of gas dissolution by diffusion, the most important property is the diffusion coefficient under the reservoir conditions. However, there is still a lack of sufficient experimental data on diffusion coefficients at high pressures especially for multicomponent mixtures and reservoir fluids.

First measurements of diffusion coefficients in hydrocarbon systems were performed by Hill and Lacey (1934) and later by Reamer et al. (1956) for the methane–decane system. Later, Woessner et al. (1969), McKay (1971), Lo (1974), Sigmund (1976), Denoyelle and Bardon (1984) and Renner (1988) reported some experimen-

tal measurements for hydrocarbon and petroleum systems at high pressures. Most of the data reported by these investigators are limited to pressures much lower than actual pressures in petroleum reservoirs due to equipment limitations.

Most conventional methods of measuring diffusion coefficients require compositional analyses which are both expensive and time-consuming (Sigmund, 1976; Hanssen and Stenberg, 1987; Riazi and Whitson, 1988; Dickson and Johnson, 1988). In addition, due to various approximations made for the models used in the calculation of diffusion coefficients from experimental data, significant errors may be associated with reported values of diffusion coefficients for multicomponent mixtures at high pressures (Riazi and Whitson, 1988). This is the main reason for significant differences reported for diffusion coefficients measured for the same system. For example, Sigmund (1976) reports a value of $30 \times 10^{-9} \text{ m}^2/\text{s}$ for the diffusion coefficient of the C_1 – C_3 system at 311 K (100°F) and 73.7 bar (1069 psia), while Graue (1965) reports $7 \times 10^{-9} \text{ m}^2/\text{s}$ for the same system under the same conditions. This difference is even larger for the case of liquid systems at high pressures. Extrapolation of available data to high pressure through existing correlations may not be accurate. Most correlations are developed based on data available on binary diffusion coefficients of relatively light compounds at high pressures. A summary of available experimental data and various methods of predicting diffusion coefficients for reservoir fluids is given by Riazi and Whitson (1993).

In general, methods used to measure diffusion coefficients in hydrocarbon systems can be divided into two categories. In the first category, during the experiment samples of the fluid are taken at various times and are analyzed by gas chromatography or other analytical tools. For example, methods used by Berry and Koeller (1960), Sigmund (1976) and Dickson and Johnson (1988) are in this category. In the second category, samples are not analyzed but self-diffusion coefficients are measured by equipments such as NMR and then correlations as those proposed by Vignes (1966) have been used to obtain binary diffusion coefficients. Methods used by Dawson et al. (1970) and Woessner et al. (1969) are in this category. Denoyelle and Bardou (1984) and Renner (1988) measured volume of gas dissolved in oil versus time at constant pressure in order to determine diffusion coefficients in reservoir fluids.

In the present paper a method is proposed to determine diffusion coefficients using a constant-volume constant-temperature PVT cell. When a non-equilibrium gas is brought into contact with a liquid in a constant-temperature, constant-volume vessel, the system approaches its equilibrium state. However, the time required for the system to reach its final equilibrium state depends on the diffusion coefficient of components in the system. The major assumption in our proposed model is that at all times, equilibrium exists between liquid and gas phases at their interface. Velocity of interface movement, as well as the rate of change in pressure of the system depend on the rate of diffusion in each phase. If correct values for diffusion coefficients of all components are used in the proposed model, then the predicted rate of interface movement should be consistent with experimental results. Therefore, there is no need for direct compositional measurement. This is the major advantage of this technique over conventional methods based on composition analysis versus time.

The main objective of this work is to develop a model which can predict the gas–liquid interface position and pressure in a constant-volume cell as the time elapses. Using measured pressure or interface position, a correct value of diffusion coefficient can be extracted from the proposed model. To evaluate the proposed method, the diffusion coefficient of methane in *n*-pentane has been measured at 70 bar and compared with the literature value.

2. Proposed experimental method

Consider a constant-volume cell shown in Fig. 1, containing non-equilibrium gas and liquid (oil) mixtures with known initial compositions. The temperature of the system can be maintained constant throughout the experiment. However, pressure, volume and composition of each phase will change with time as the system

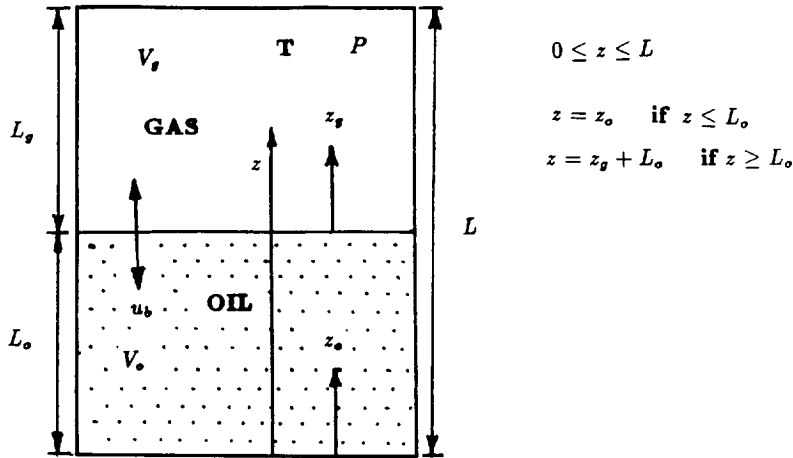


Fig. 1. Schematic and dimensions of a constant-volume cell.

approaches its equilibrium state. In general, a model will be developed for the multicomponent-gas/multicomponent-liquid hydrocarbon systems.

2.1. Mathematical formulation

For the system shown in Fig. 1, mole fraction of component i in the oil phase is x_i and in the gas phase is y_i . Molar concentration C and absolute density ρ in each phase can be calculated from an equation of state (EOS). We use subscript g for the gas phase and subscript o for the liquid/oil phase. Total moles of component i in the system is shown by n_i and the total mass is shown by m_i . For an N component system with oil volume fraction S_o basic parameters for the liquid phase can be calculated from the set of equations given in Table 1. The relations for the gas phase are similar to those for the liquid phase. Relations for calculation of the total moles n and the total mass m in the system are also given in Table 1. F_v is the mole fraction of the gas phase in the system and it can be calculated from equations given in Table 1. Since material does not leave the system, total mass m and the total moles in the system n remain constant throughout the experiment. The heights of liquid and gas in the cell, L_o and L_g , as shown in Fig. 1, can be estimated from the cross-sectional area of the cell A as given in Table 1. Due to the importance of notations used throughout the text, complete definitions of all parameters used in this article are given in the nomenclature section.

When there is a concentration gradient in the gas and liquid phases, diffusion will take place in both phases. The governing differential equation which describes the diffusion process in each phase shown in Fig. 1 is given by Fick's second law. For the coordinate system shown in Fig. 1 and for the oil phase this equation is:

$$\frac{\partial C_{oi}}{\partial t} - u_o \frac{\partial C_{oi}}{\partial z_o} = \frac{\partial}{\partial z_o} \left[D_{oi} \frac{\partial C_{oi}}{\partial z_o} \right] \tag{1}$$

Use of Fick's law to describe the diffusion in dense fluids can be justified by considering that the diffusion coefficient should be corrected by a thermodynamic factor for non-ideal mixtures:

$$D_{oi} = D_{oi} \left(1 + \frac{\partial \ln \phi_i}{\partial \ln x_i} \right) \tag{2}$$

where ϕ_i is the fugacity coefficient of component i in the mixture. For ideal mixtures and for dilute systems the thermodynamic correction factor $(1 + \frac{\partial \ln \phi_i}{\partial \ln x_i})$ is unity and both D_{oi} and \mathbf{D}_{oi} are equal.

Table 1
Calculation of model parameters in Fig. 1

$$V = V_o + V_g$$

$$S_g = \frac{V_g}{V_o + V_g}$$

$$S_o = \frac{V_o}{V} = 1 - S_g$$

$$M_o = \sum_{i=1}^N x_i M_i$$

$$\rho_o = M_o \times C_o$$

$$C_{oi} = x_i C_o$$

$$n_{oi} = V_o \times C_{oi}$$

$$m_{oi} = n_{oi} \times M_i$$

$$n_o = \sum_{i=1}^N n_{oi}$$

$$m_o = \sum_{i=1}^N m_{oi}$$

$$n_i = n_{oi} + n_{gi}$$

$$m_i = m_{oi} + m_{gi}$$

$$n = \sum_{i=1}^N n_i = n_o + n_g$$

$$m = \sum_{i=1}^N m_i = m_o + m_g$$

$$F_V = \frac{n_g}{n}$$

$$L = \frac{V}{A}$$

$$L_o = \frac{V_o}{A}$$

$$L_g = L - L_o = S_g \times L = \frac{V_g}{A}$$

T , V , and L are constant while P , V_o , V_g , L_o and L_g vary with time.

The second term in the left hand side of Eq. 1 is the convection term, and the negative sign implies that the velocity u_o is in the opposite direction of the z -axis. When density of liquid phase is decreasing with gas dissolution, as it is in the case of this study, the free convection does not occur and Eq. 1 reduces to:

$$\frac{\partial C_{oi}}{\partial t} = \frac{\partial}{\partial z_o} \left[D_{oi} \frac{\partial C_{oi}}{\partial z_o} \right] \quad (3)$$

The boundary conditions are:

$$\begin{aligned} at \quad t = 0 \quad C_{oi} &= C_{oi}^1 \\ at \quad z_o = 0 \quad \frac{\partial C_{oi}}{\partial z_o} &= 0 \\ at \quad z_o = L_o \quad C_{oi} &= C_{obi} \end{aligned}$$

in which C_{oi}^1 is the initial concentration of component i in the liquid phase and C_{obi} is the boundary concentration in the liquid. In the above equations C_{obi} and L_o vary with time. Inasmuch as L_o varies with time we choose a time step Δt during which L_o can be considered constant in the diffusion equation. However, for the next time interval a new value of L_o should be used. In the next time interval, the initial concentration C_{oi}^1 should also be replaced with its value at the end of the previous time step C_{oi}^T . Obviously, C_{oi}^1 is constant along

the axis z_0 while C_{oi}^T is a function of z_0 . Eq. 3 with the corresponding conditions can also be applied to the gas phase using appropriate notations.

To solve the above differential equation, it is more convenient to convert all parameters into dimensionless form designated by an asterisk. For example, $C_{oi}^* = \frac{C_{oi} - C_{gi}^T}{C_{oi}^T - C_{gi}^T}$, can be used instead of C_{oi} . Eq. 3, in a dimensionless form, for the liquid phase has the following form:

$$\frac{\partial C_{oi}^*}{\partial t_{oi}^*} = \frac{\partial^2 C_{oi}^*}{\partial z_0^{*2}} \tag{4}$$

where $t_{oi}^* = \frac{D_{oi}t}{L_o^2}$ and $z_0^* = \frac{z_0}{L_o}$.

The corresponding boundary conditions are:

$$\begin{aligned} \text{at } t^* = 0 \quad C_{oi}^* &= C_{oi}^{*T} \\ \text{at } z_0^* = 0 \quad \frac{\partial C_{oi}^*}{\partial z_0^*} &= 0 \\ \text{at } z_0^* = 1 \quad C_{oi}^* &= C_{obi}^* \end{aligned}$$

In deriving this dimensionless form from Eq. 4, it was necessary to assume that during each time interval, D_{oi} is constant. This assumption can be justified by choosing a small time interval and evaluating the diffusion coefficient with its thermodynamic correction factor from the compositions obtained at the end of the previous time steps.

The dimensionless form of Eq. 3, applied to the gas phase shown in Fig. 1, is:

$$\frac{\partial C_{gi}^*}{\partial t_{gi}^*} = \frac{\partial^2 C_{gi}^*}{\partial z_g^{*2}} \tag{5}$$

where $t_{gi}^* = \frac{D_{gi}t}{L_g^2}$, $z_g^* = \frac{z_g}{L_g}$ and $C_{gi}^* = \frac{C_{gi} - C_{oi}^T}{C_{oi}^T - C_{gi}^T}$

A similar thermodynamic factor as shown in Eq. 2 is also applied to estimate gas phase diffusion coefficients. The corresponding boundary conditions are:

$$\begin{aligned} \text{at } t_{gi}^* = 0 \quad C_{gi}^* &= C_{gi}^{*T} \\ \text{at } z_g^* = 0 \quad C_{gi}^* &= C_{gbi}^* \\ \text{at } z_g^* = 1 \quad \frac{\partial C_{gi}^*}{\partial z_g^*} &= 0 \end{aligned}$$

In the above equations t does not represent cumulative time but varies from 0 to the chosen time step Δt . The cumulative time is obtained from the summation of these time steps. As mentioned earlier, only at the first time step the initial condition is $C_i^* = C_i^{*T}$ and for the subsequent time intervals the initial condition becomes $C_i^* = C_i^{*T}$. After the first time step, C_i^{*T} is a function of z^* . The exact form of this function is known from the solution of Eqs. 4 and 5 at the end of each time step. During this small time interval chosen for the calculations, diffusion coefficients are assumed to be constant and are evaluated at average concentrations at the end of the previous time step. Therefore, the following solutions can be obtained for Eqs. 4 and 5 and are valid only during each time interval period.

$$C_{oi}^* = C_{obi}^* + 2 \sum_{n=1}^{\infty} (P_{ni} - C_{obi}^*) \lambda_n \exp(-\lambda_n^2 t_{oi}^*) \cos(\lambda_n z_0^*) \tag{6}$$

$$C_{gi}^* = C_{gbi}^* - 2 \sum_{n=1}^{\infty} \frac{(C_{gbi}^* - Q_{ni})}{\lambda_n} \exp(-\lambda_n^2 t_{gi}^*) \sin(\lambda_n z_g^*) \tag{7}$$

where:

$$\lambda_n = (2n - 1) \frac{\pi}{2} \quad (n = 1, 2, 3, 4, 5, \dots, \alpha)$$

$$\lambda_n^1 = \frac{(-1)^{n+1}}{\lambda_n}$$

Parameters P_{ni} and Q_{ni} are defined by the following expressions:

$$P_{ni} = \frac{1}{\lambda_n^1} \int_0^1 C_{oi}^{*T}(z_o^*) \cos(\lambda_n z_o^*) dz_o^* \quad (8)$$

$$Q_{ni} = \lambda_n \int_0^1 C_{gi}^{*T}(z_g^*) \sin(\lambda_n z_g^*) dz_g^* \quad (9)$$

where $C_{oi}^{*T}(z_o^*)$ and $C_{gi}^{*T}(z_g^*)$ are concentration profiles obtained from Eqs. 6 and 7 at the end of the previous time step. Substitution of Eqs. 6 and 7 into Eqs. 8 and 9 would result in the following expressions for parameters P_{ni} and Q_{ni} at the beginning of each new time step:

$$P_{ni} + C_{obi}^{*T} + \frac{1}{\lambda_n^1} \sum_{m=1}^{\infty} \alpha_{mn} (P_{mi}^T - C_{obi}^{*T}) \lambda_m^1 \exp(-\lambda_m^2 t_{oi}^*) \quad (10)$$

$$Q_{ni} = C_{gbi}^{*T} - \lambda_n \sum_{m=1}^{\infty} \beta_{mn} \frac{(C_{gbi}^{*T} - Q_{mi}^T)}{\lambda_m} \exp(-\lambda_m^2 t_{gi}^*) \quad (11)$$

where the parameters α_{mn} and β_{mn} are defined in the following forms:

If $m \neq n$

$$\alpha_{mn} = \frac{1}{\lambda_m - \lambda_n} \sin(\lambda_m - \lambda_n) + \frac{1}{\lambda_m + \lambda_n} \sin(\lambda_m + \lambda_n)$$

and

$$\beta_{mn} = \frac{1}{\lambda_m - \lambda_n} \sin(\lambda_m - \lambda_n) - \frac{1}{\lambda_m + \lambda_n} \sin(\lambda_m + \lambda_n)$$

If $m = n$

$$\alpha_{mn} = \beta_{mn} = 1$$

in which λ_m and λ_m^1 are defined in the same way as λ_n and λ_n^1 . Superscript T indicates that the specified property is evaluated at the end of the previous time step. The average molar concentrations can be obtained by integrating Eqs. 6 and 7 from 0 to 1 with respect to z^* , which results in the following relations:

$$C_{oai}^* = C_{obi}^* + 2 \sum_{n=1}^{\infty} \frac{(P_{ni} - C_{obi}^*)}{\lambda_n^2} \exp(-\lambda_n^2 t_{oi}^*) \quad (12)$$

$$C_{gai}^* = C_{gbi}^* - 2 \sum_{n=1}^{\infty} \frac{(C_{gbi}^* - Q_{ni})}{\lambda_n^2} \exp(-\lambda_n^2 t_{gi}^*) \quad (13)$$

In the above equations the boundary concentrations, C_{obi}^* and C_{gbi}^* , are yet to be determined. Calculation of these boundary concentrations will be discussed shortly.

Once average concentrations of each component in each phase are determined from Eqs. 12 and 13, mole fractions x_i and y_i in the liquid and gas phases can be estimated using the following relations:

$$x_i = \frac{C_{oi}^* (C_{oi}^1 - C_{gi}^1)}{\sum_{i=1}^N C_{oi}^* (C_{oi}^1 - C_{gi}^1)} = \frac{C_{oi}}{C_o} \tag{14}$$

$$y_i = \frac{C_{gi}^* (C_{oi}^1 - C_{gi}^1)}{\sum_{i=1}^N C_{gi}^* (C_{oi}^1 - C_{gi}^1)} = \frac{C_{gi}}{C_g} \tag{15}$$

As mentioned earlier the main task in the estimation of compositions in each phase through the above equations is to determine the concentrations at the liquid–gas boundary.

From the law of conservation of mass, two fluxes on both sides of the interface should be equal:

$$-D_{oi} \frac{\partial C_{oi}}{\partial z_o} + u_b C_{obi} = -D_{gi} \frac{\partial C_{gi}}{\partial z_g} + u_b C_{gbi} \tag{16}$$

in which u_b is the velocity of moving liquid–gas interface. In fact u_b represents the variation of height of liquid phase (L_o) with respect to time. In Eq. 16 derivatives of C_{oi} and C_{gi} are calculated from Eqs. 6 and 7. At the liquid–gas interface, we can assume an equilibrium state to exist between liquid and gas phases, that is:

$$f_{oi} = f_{gi} \tag{17}$$

where f_{oi} and f_{gi} are the fugacities of component i in liquid and gas at the interface. These thermodynamic properties can be calculated from an equation of state (EOS). The above equation can also be written in the following form:

$$y_{bi} = K_i x_{bi} \tag{18}$$

where K_i is the equilibrium ratio of component i and can be determined from fugacity coefficients calculated from an equation of state. As pressure in the system and the boundary composition change, these equilibrium ratios also change. This equation can be converted into the following form in terms of boundary concentrations:

$$C_{gbi}^* = R_C K_i C_{obi}^* \tag{19}$$

where

$$R_C = \frac{C_{gb}}{C_{ob}} = \frac{\sum_{i=1}^N C_{gbi}^* (C_{oi}^1 - C_{gi}^1)}{\sum_{i=1}^N C_{obi}^* (C_{oi}^1 - C_{gi}^1)} \tag{20}$$

From simultaneous solution of Eqs. 16 and 19, C_{obi} can be determined. In a dimensionless form:

$$C_{obi}^* = \frac{\sum_{n=1}^{\infty} Q_{ni} \exp(-\lambda_n^2 t_{gi}^*) + R_i \sum_{n=1}^{\infty} P_{ni} \exp(-\lambda_n^2 t_{oi}^*)}{K_i R_C \sum_{n=1}^{\infty} \exp(-\lambda_n^2 t_{gi}^*) + R_i \sum_{n=1}^{\infty} \exp(-\lambda_n^2 t_{oi}^*) + \frac{R_i}{2} (K_i R_C - 1) u_b^*} \tag{21}$$

where:

$$R_i = \left(\frac{D_{oi}}{D_{gi}} \right) \times \left(\frac{L_g}{L_o} \right)$$

and:

$$u_b^* = \frac{L_g u_b}{D_{oi}}$$

λ_n , P_{ni} , and Q_{ni} are defined in Eqs. 6 and 7. In Eq. 21, the parameter R_C , which is the concentration ratio at the boundary, can be obtained by trial and error. Details of the calculation procedure will be discussed later. C_{gbi}^* can be calculated directly from Eq. 19.

In the above diffusion equations, the effective diffusion coefficient of component i in the liquid and gas mixtures is the most important property which determines the time required for the system to reach its final equilibrium state. Not many accurate and general correlations are available in the literature for estimation of these coefficients. One of the correlations developed for diffusion coefficients in reservoir fluids is the Sigmund (1976) correlation for binary dense fluids; we will use this correlation in our calculations because of its simplicity. Sigmund's correlation is in the form of a reduced density–diffusivity product as a function of mixture reduced density. It is relatively accurate for gases; however, for dense liquids it may cause errors of up to 50%. Once the binary diffusion coefficients were calculated through Sigmund's correlation, Wilke's method (Wilke, 1950) has been used for estimation of effective diffusion coefficient of component i in a multicomponent mixture. A recent method proposed by Riazi and Whitson (1993) for estimation of diffusion coefficients of dense fluids in terms of viscosity will also be used for comparison.

2.2. Calculation procedure

For the application of the model developed in this work, one main condition to be satisfied is equality of fugacities for each component in gas and liquid phases at the boundary expressed by Eq. 17. A fugacity deviation parameter E_f can be defined as:

$$E_f = \sum_{i=1}^N \left(1 - \frac{f_{gi}}{f_{li}}\right)^2 \quad (22)$$

K_i values used in Eq. 18 should be estimated through fugacity coefficients which gives a minimum value ($\leq 10^{-5}$) for E_f in the above equation.

Another important criterion in the proposed model is that the material balance for each component must be satisfied throughout the calculations. That is the total mass of component i in the cell from Table 1, m_i , must be constant at any time t .

The initial input data necessary to start the calculations are: volume of the cell (V); cross-sectional area of the cell (A); initial composition of the liquid and gas phases (x_i^l and y_i^g); initial oil saturation (S_o), temperature (T), and initial pressure (P) of the system. The time step (Δt) must be chosen to be appropriate to dimensions of the system. For example, for L_o of 6 to 7 cm, $\Delta t = 30$ min is suitable and for larger systems it may increase proportionally with the square of the dimension (L_o^2). To calculate the boundary concentrations from Eq. 21, a trial-and-error procedure is required to estimate parameter R_c defined by Eq. 20. However, during each round of calculations, the boundary concentrations, C_{ob} and C_{gb} , should be consistent with those estimated through an equation of state. Calculations must be ended when there is no change in compositions and no other properties for both gas and liquid phases. At this stage compositions (x_i and y_i), pressure (P) and volumes (V_o and V_g) should be the same as those estimated through constant-volume flash calculation using an equation of state.

In systems in which the liquid density at the bottom of the cell is greater than at the liquid–gas interface, there is no need to consider natural convection because velocity u_o in Eq. 1 is zero. Also for systems with very small density gradients the velocity is not very high and Eq. 3 may be used instead of Eq. 1. Perhaps the most convenient way of solving Eq. 1 with the associated equations and boundary conditions would be by numerical techniques. However, when $u = 0$, the solution should reduce to the one presented in this work for the case of no convection.

It is quite convenient to check the existence of natural convection in each phase in a vertical cell. At early times, the density of the liquid phase at the bottom of the cell is very close to the initial density of the liquid phase, while the boundary density is closer to the final density. Therefore, for the liquid phase, if the final density is less than its initial value, convection does not exist during the diffusion process. Similarly, if the initial density of gas is less than its final value, convection does not occur in the gas phase.

3. Evaluation of the proposed technique

To evaluate the proposed technique of experimental measurement of diffusion coefficients in dense fluids, the system of methane (C_1) and normal pentane (nC_5) at a temperature of 37.8°C (100°F) and an initial pressure of 102 bar (1480 psia) is considered here for the experiment. Major reasons for choosing this system are:

1. Experimental data are available in the literature.
2. Temperature and pressure are easily obtained with existing laboratory equipments.
3. The time required for the system to reach its final state is about one week, and experimental results can be obtained and analyzed within the first few days.
4. Changes in the interface position and pressure are relatively large, so they can represent the rate of mass transfer with reasonable accuracy.
5. For the case of vertical cells, convection does not occur in the liquid phase due to the negative density gradient in the z -direction (Fig. 1) and decreasing density in the liquid phase by gas dissolution.

3.1. Experimental procedure

A visual sapphire PVT cell at IKU (Institute for Continental Shelf Research) was used. The height and the diameter of the cell were 21.943 and 2.56 cm, respectively. The system initially contained pure components as vapour methane and liquid pentane. Initially the cell was partially filled (35% by volume) with normal pentane. Vacuum was applied, and the liquid volume at saturated conditions was made to determine the moles of n -pentane initially. High pressure methane was introduced slowly until the pressure reached 102 bar (requiring about one minute). At this point the experiment began, registering pressure, temperature, and liquid level as a function of time. Pressures were recorded manually at selected times, and continuously on a strip chart. The liquid level was measured manually with a precision of ± 0.02 mm.

3.2. Calculations

Before simulating the diffusion experiment, the PVT behaviour of the initial pure components and final equilibrium mixture were calculated with the Peng–Robinson EOS. The fluid characterization was slightly

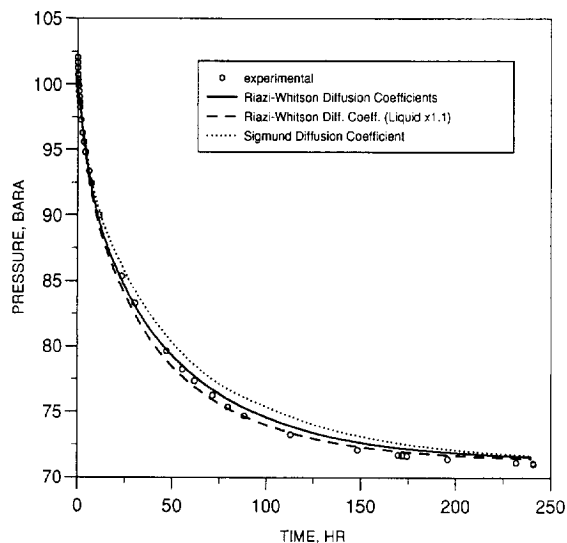


Fig. 2. Variation of pressure for the C_1-nC_5 constant-volume diffusion experiment at 37.8°C.

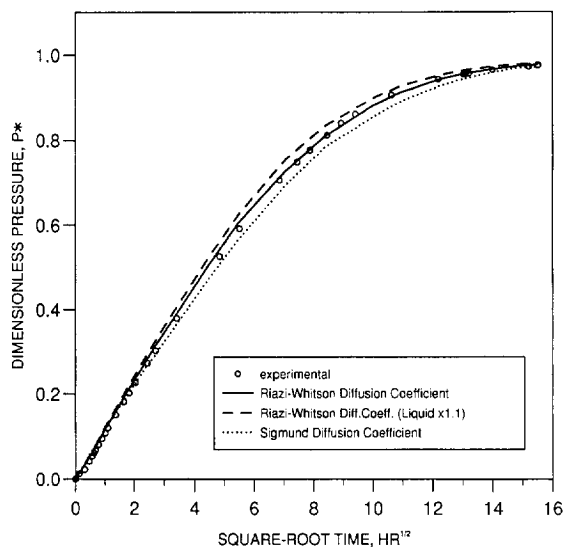


Fig. 3. Variation of dimensionless pressure for the C_1-nC_5 constant-volume diffusion experiment at 37.8°C .

modified, and volume shift parameters of -0.2044 and -0.045 were used for methane and n -pentane, respectively. A binary interaction coefficient of 0.054 was used in the calculations. Pure compound densities at initial conditions were used to determine volume translation coefficients, and the interaction coefficient was modified to match the final liquid volume fraction. Calculated final equilibrium gas compositions were $y_1 = 95.43\%$, $y_5 = 4.57\%$, compared with measured values of $y_1 = 94.92\%$, $y_5 = 5.08\%$, confirming the validity of EOS used for phase equilibrium calculations.

In order to further reduce errors caused by use of an equation of state, it is more appropriate to present the pressure and the liquid level in reduced quantities. Parameters P^* and L_0^* are defined in the following forms

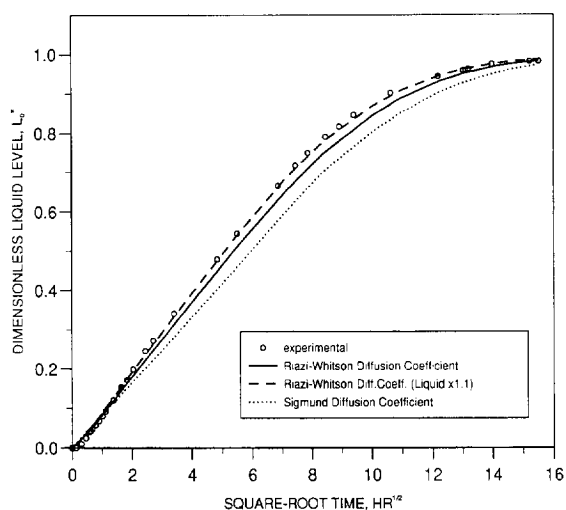


Fig. 4. Variation of dimensionless liquid level versus time for the C_1-nC_5 constant-volume diffusion experiment at 37.8°C .

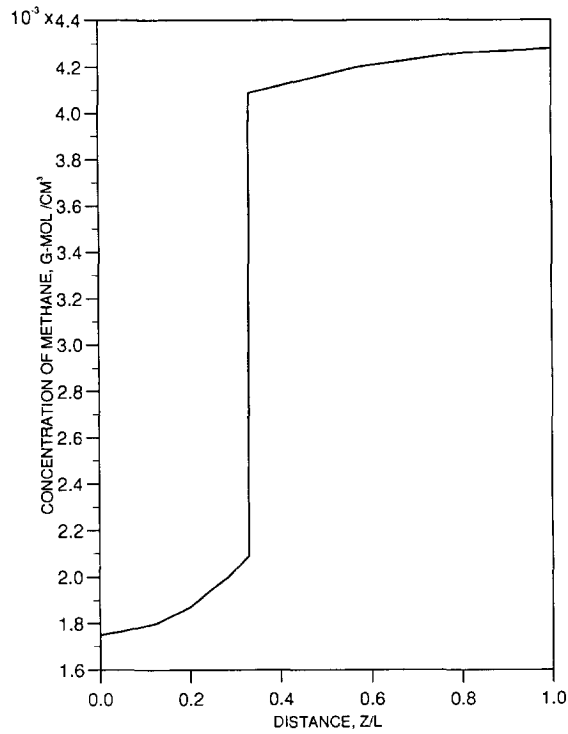


Fig. 5. Concentration profile of methane after 28 h for the C_1-nC_5 constant-volume diffusion experiment at 37.8°C .

for presentation of fractional changes in pressure and interface position with respect to the total changes during the entire diffusion period:

$$p^* = \frac{P^I - P}{P^I - P^\infty} \tag{23}$$

$$L_o^* = \frac{L_o - L_o^I}{L_o^\infty - L_o^I} \tag{24}$$

Subscripts I and ∞ represent the initial and final states, respectively.

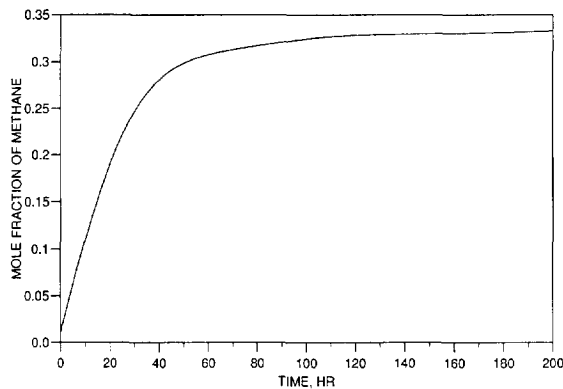


Fig. 6. Mole fraction of methane in the liquid phase for the C_1-nC_5 constant-volume diffusion experiment at 37.8°C .

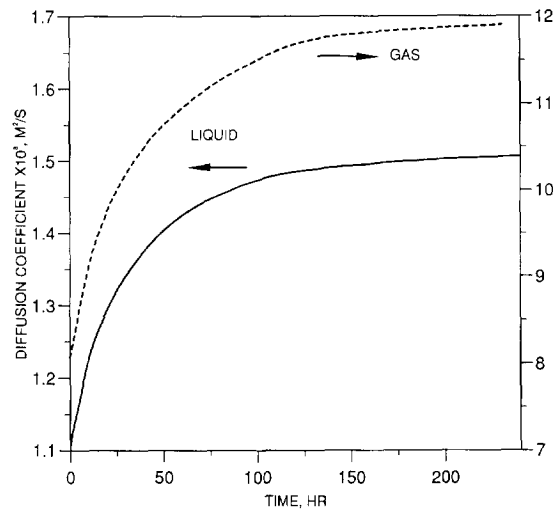


Fig. 7. Diffusion coefficient of the methane–*n*-pentane system at 37.8°C for the liquid and gas phases.

Three simulations of the experiment were conducted using the semi-analytical model proposed in the previous section. Results from these calculations are shown in Figs. 2–4, where the following diffusion coefficient correlations were used: the Riazi–Whitson (1993) correlation; the Riazi–Whitson (1993) correlation with liquid values multiplied by 1.1; and the Sigmund (1976) correlation.

The model results are very similar to experimental results, thereby confirming both the proposed mathematical model, and the assumption that diffusion dominates the mass transfer in such systems.

For estimating the diffusion coefficient, the composition of each phase must be used. Compositions vary along the *z*-axis (see Fig. 1) and, therefore, diffusion coefficients are functions of distance *z*. Diffusion mainly occurs in the region close to the gas–liquid interface. In our calculations the boundary composition was used for estimating the diffusion coefficients used for evaluation of fluxes at the interface (Eq. 16), while the arithmetic average composition based on the bulk composition and the boundary composition was used for estimating diffusivities used in the calculation of concentration profiles. The methane concentration profile in the cell is shown in Fig. 5 after 28 h. The methane composition in the liquid phase is shown in Fig. 6 and diffusion coefficients calculated from the Riazi–Whitson correlation for both phases are shown in Fig. 7. A correlation factor of 1.1 as discussed before has been used for the liquid phase diffusion coefficients. The diffusion coefficient of methane in liquid *n*-pentane is a strong function of the methane composition. Toward the end of the experiment where the pressure reaches 71 bar and methane mole fraction becomes 0.33, the diffusion

Table 2

Liquid diffusion coefficients of the methane–*n*-pentane system

Temperature:	37.8°C (100°F)
Pressure:	71 bar
Mole fraction of methane:	0.33
Riazi–Whitson (1993)	$1.37 \times 10^{-8} \text{ m}^2/\text{s}$
Riazi–Whitson (1993) $\times 1.1$	^a $1.51 \times 10^{-8} \text{ m}^2/\text{s}$
Sigmund (1976) correlation	$1.22 \times 10^{-8} \text{ m}^2/\text{s}$
Reamer–Duffy–Sage (1956) (exp.)	$1.43 \times 10^{-8} \text{ m}^2/\text{s}$

^a This is the value obtained from the experimental technique proposed in this study.

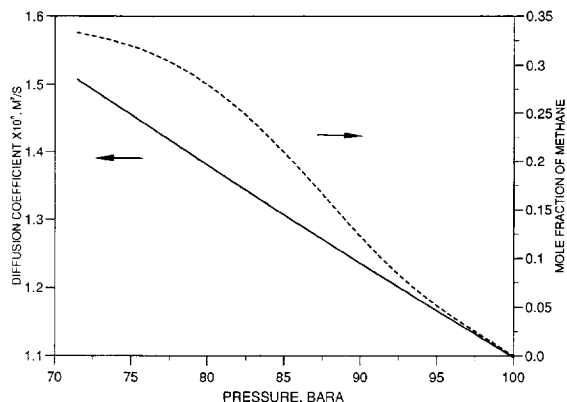


Fig. 8. Diffusion coefficient of the liquid phase methane–*n*-pentane system at 37.8°C versus pressure and composition.

coefficient from the Riazi–Whitson correlation is $1.37 \times 10^{-8} \text{ m}^2/\text{s}$ (or 1.51 in Fig. 7) and the Sigmund correlation is $1.2 \times 10^{-8} \text{ m}^2/\text{s}$.

As shown in Fig. 4, the best values for the diffusion coefficients can be obtained by multiplying liquid diffusion coefficients from the Riazi–Whitson method by 1.1, which gives a value of $1.51 \times 10^{-8} \text{ m}^2/\text{s}$ at 71 bar. Under these conditions the experimental value of the diffusion coefficient for the C_1 – nC_5 liquid system reported by Reamer et al. (1956) and shown in Table 2 is 1.43×10^{-8} , giving a deviation of only 5% from the proposed method in this work.

The major advantage of this technique over other conventional methods is that due to the reasonable assumptions made in the modelling of the problem, a good match between experimental results and model predictions can be obtained for the entire range of experimental data. In many other conventional methods due to the nature of approximations made during the formulation of the problem, only a fraction of experimental data were used to obtain diffusion coefficients (Dickson and Johnson, 1988). This problem is the reason that experimental data should be obtained for a very long period of time. As it is seen from Figs. 3 and 4, a good estimate of the diffusion coefficient can be obtained from experimental data at the first 10–15 h of the experiment. This period for running the experiment can be further reduced if initial height of liquid level in the cell is required. This indicates that all values of diffusion coefficients shown in Fig. 7 at any time are correct. Another advantage of this method is that diffusion coefficients of the gas phase can also be determined simultaneously with the liquid phase diffusion coefficient at various compositions and pressures. A set of diffusion coefficients for both gas and liquid phases at various pressures and compositions can be obtained from the simultaneous use of Figs. 2 and 6 and 7. This would greatly save time and money in measuring diffusion coefficients at high pressures. Diffusion coefficients of methane–*n*-pentane in the liquid phase versus pressure and composition at 37.8°C (100°F) are shown in Fig. 8. The diffusion coefficient decreases with pressure almost linearly for the composition given in Fig. 8. The proposed method can be used as a basis for measurement of effective diffusion coefficients in reservoir fluids (gas–gas, gas–liquid, liquid–liquid) and multicomponent systems from simple experiments. This would be the next phase of this study.

4. Conclusions

The following conclusions can be drawn from the work presented in this paper:

1. In this work a semi-analytical model has been developed for the estimation of mass transfer rates caused by diffusion between a non-equilibrium gas and liquid in a constant volume cell with constant temperature.
2. In the proposed model, composition of each phase, pressure of the system and volume of each phase can be calculated versus time.

3. Results from diffusion equations as $t \rightarrow \infty$ agree well with those obtained from constant-volume flash calculations.
4. Diffusion coefficients in both liquid and gas phases can be measured by using a PVT cell and measuring the change of pressure and/or liquid level versus time at constant temperature.
5. The experimental results for the C_1 – nC_5 system from this study are within $\pm 5\%$ of literature values.
6. In the proposed method of measuring diffusion coefficients no compositional measurements are necessary; hence, it is less expensive and more accurate than conventional techniques.
7. Using the method proposed in this paper, one can obtain a set of diffusion coefficient data for both gas and liquid phases at various pressures and compositions by setting only one experiment.

5. Nomenclature

A	= Cross-sectional area of the cell.
C_o	= Molar density (concentration) of oil.
C_g	= Molar density (concentration) of gas.
C_{oi}	= Molar concentration of component i in oil.
C_{gi}	= Molar concentration of component i in gas.
C_{oi}^*	= Dimensionless concentration of component i in oil defined as $[= \frac{C_{oi}}{(C_{oi}^* - C_{gi}^*)}]$.
C_{oi}^I	= Initial molar concentration of component i in oil.
C_{oi}^T	= Molar concentration of component i in oil at the beginning of each new time step.
C_{oi}^{inf}	= Final equilibrium concentration of component i in oil.
C_{obi}	= Molar concentration of component i in oil at the liquid–gas boundary.
C_{oi}^*	= Average dimensionless concentration of component i in oil defined in Eq. 12.
D_{gi}	= Effective diffusion coefficient of component i in gas.
D_{oi}	= Effective diffusion coefficient of component i in oil.
D_{oi}	= Maxwell–Stefan diffusion coefficient of component i in oil.
E_f	= Parameter defined in Eq. 22.
F_o	= Mole fraction of oil phase in the cell $[= 1 - F_v]$.
F_g	= Mole fraction of gas phase in the cell.
g	= Acceleration of gravity.
K_i	= Equilibrium ratio of component i $[= \frac{x_i}{y_i}]$.
L_o	= Length of the liquid phase defined in Fig. 1.
L_g	= Length of the gas phase defined in Fig. 1.
L_o^*	= Dimensionless length of the liquid phase defined in Eq. 24.
M	= Molecular weight.
M_o	= Molecular weight of the oil phase.
m	= Total mass of all components in the cell.
m_o	= Total mass of all components in the oil/liquid phase.
N	= Total number of all components in the system.
n_o	= Total moles of all components in the oil phase.
P	= Pressure.
P^*	= Dimensionless pressure defined by Eq. 23.
P_{ni}	= A parameter defined in Eq. 8 for component i and n th eigenvalue.
Q_{ni}	= A parameter defined in Eq. 9 for component i and n th eigenvalue.
R_C	= Gas–oil concentration ratio at the boundary defined in Eq. 20.
R_i	= A dimensionless parameter defined in Eq. 21.

S_o	= Oil saturation defined in Table 1.
T	= Temperature.
t	= Time.
t_{oi}^*	= Dimensionless time for component i in oil defined as $[= \frac{D_{oi}t}{L_o^2}]$.
u_b	= Velocity of liquid–gas interface defined as $[= \frac{\partial L_o}{\partial t}]$.
u_b^*	= Dimensionless boundary velocity defined as $[= \frac{L_o u_b}{D_{oi}t}]$.
u_o	= Oil velocity caused by natural convection.
V	= Total volume of the cell.
V_g	= Volume of gas in the cell.
V_o	= Volume of oil in the cell.
x_i	= Mole fraction of component i in liquid defined in Eq. 14.
x^*	= Dimensionless distance defined as $[= \frac{x}{L_o}]$.
y_i	= Mole fraction of component i in gas defined in Eq. 15.
z	= Axis for diffusion in the cell as defined in Fig. 1.
z_o	= Axis for diffusion in oil in the model as defined in Fig. 1.
z_g	= Axis for diffusion in gas in the model as defined in Fig. 1.
z^*	= Dimensionless axis defined as $[= \frac{z}{L}]$.
z_o^*	= Dimensionless axis defined as $[= \frac{z_o}{L_o}]$.

Greek letters:

α_{mn}	= Parameter defined in Eq. 10.
β_{mn}	= Parameter defined in Eq. 11.
Δt	= Time step.
λ_n	= n th eigenvalue defined in Eqs. 6 and 7.
λ_n^1	= Modified n th eigenvalue defined in Eqs. 6 and 7.
ρ_o	= Mass density of the liquid phase.
ρ_g	= Mass density of the gas phase.
ϕ_i	= Fugacity coefficient of component i in mixture.

Subscripts:

a	= average concentration values
b	= values at the oil–gas boundary
g	= gas phase
i	= component i
o	= oil phase

Superscripts:

*	= dimensionless parameters
I	= initial values
T	= values at the beginning of each new time step
∞	= values at the final equilibrium condition

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