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Determination of diffusion coefficients from constant volume diffusion tests through numerical simulation

Check for updates

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ABSTRACT

Keywords: Diffusion Equation of state Orthogonal collocation method High pressure Molecular diffusion is a fundamental mass transport phenomenon crucial to many scientific and industrial fields. Its accurate description relies on diffusion coefficients that can be either experimentally measured or theoretically estimated. The constant volume diffusion (CVD) method is a widely used approach to measure liquid-phase diffusion coefficients at high pressures. However, it requires analytical or numerical solutions to interpret the measured data. In this study, we described in detail a legacy CVD simulation code developed by Michael L. Michelsen and showed how his algorithm can determine constant or composition-dependent diffusion coefficients from the CVD data using the orthogonal collocation method. We further coupled the code with five diffusion coefficient correlations, including the Wilke-Chang (WC), Hayduk-Minhas (HM), extended Sigmund (ES), Riazi-Whitson (RW), and Leahy-Dios-Firoozabadi (LDF), to investigate their performance in terms of predicting and regressing the CVD data for methane-n-alkane and nitrogen-n-alkane systems. We found that the CVD results are insensitive to the gas-phase diffusion coefficients. The simple WC and HM give the closest predictions despite their empirical nature and inherent inconsistency. In contrast, the predictions by LDF under the rigorous Maxwell-Stefan framework are not satisfactory. The regression results using different correlations and a constant liquid-phase diffusion coefficient are almost the same. Different correlations result in different ranges of the regressed coefficients, and those determined using the assumption of constant diffusion coefficients are always within these ranges. We also compared and illustrated the differences in the profiles of diffusion coefficients between these correlations. The study demonstrates that Michelsen's algorithm is an effective tool for processing CVD data, and it also highlights how the interpretation of CVD data depends on the assumed composition-dependence.

1. Introduction

Molecular diffusion is a fundamental mass transport phenomenon that, together with convective mixing, determines the time needed for a system to reach chemical equilibrium. In situations where convective mixing is limited, the role of molecular diffusion becomes even more significant. Molecular diffusion is a critical factor in a wide range of scientific and engineering fields, such as geologic processes [1], chemical separation [2], and biomedical applications [3]. In the oil and gas production, molecular diffusion is crucial in the study of solution gas drive [4–6], the production from fractured reservoirs [7–11], the development of unconventional shale or other tight formation [12–15], and the production of highly viscous heavy oil and bitumen [16,17].

There are two major theoretical frameworks for diffusion: the Fickian framework [18] and the Maxwell-Stefan (MS) one [19], both of which provide a quantitative description of molecular diffusion. While the MS framework is theoretically rigorous, the Fickian law is more commonly used. Both frameworks use diffusion coefficients to express the diffusion rate. It should be noted that the two types of diffusion coefficients are generally not the same, and a conversion is possible under certain situations.

Experimental measurement of diffusion coefficients is indispensable but challenging, especially at elevated pressures. The review of some experimental measurement methods can be found in [20–25]. To determine liquid-phase diffusion coefficients at high pressures, the Constant Volume Diffusion (CVD) method [26,27] is often used, particularly in the oil industry. This unsteady-state method involves bringing two non-equilibrium phases (gas and liquid) into contact in a fixed volume cell at constant temperature. The pressure will vary with time during the experiment as the diffusion takes place in both phases.

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Fig. 1. Schematic of the CVD test.

The pressure typically decreases with time—that is why it is also known as the pressure decay (PD) method [27]. We use the CVD term here since an earlier study [26] already suggested it. The outcome of a CVD test includes the pressure variation with time, and, sometimes, the liquid height variation with time. The data can be processed using an analytical model [27,28] or a numerical one [26,29–32] to obtain the diffusion coefficients (mainly the liquid-phase ones).

While using an analytical model is faster, most analytical methods require some assumptions, such as a constant interface height or a simple equilibrium relation (e.g., Henry's law). These assumptions can be reasonable simplifications for some special cases, such as the diffusion in heavy oils. However, for most gas-liquid systems, a more general equilibrium description using equations of state (EoS) is necessary, and the variation of the interface height is often non-negligible. In 1992, Michael L. Michelsen developed a general CVD algorithm based on the orthogonal collocation method [26], but the work does not seem to be widely known among the researchers in this area. His method describes the gas and liquid phases using a cubic EoS and the instantaneous equilibrium at the interface by rigorous fugacity equalities. The method allows for a moving interface and composition-dependent diffusion coefficients. However, the method was only briefly described in the literature [26,33]. In this study, we intend to provide the details of Michelsen's algorithm and couple his code [34] with different diffusion coefficient models to investigate the processing of the CVD data.

In the literature, various diffusion coefficient correlations are available, and for this study, we have chosen five widely-used correlations: the Wilke-Chang (WC) correlation [35], the Hayduk-Minhas (HM) correlation [36], the extended Sigmund (ES) correlation [37,38], the Riazi-Whitson (RW) correlation [39], and the Leahy-Dios-Firoozabadi (LDF) correlation [40]. WC and HM were developed based on the Stokes-Einstein theory [41,42] for liquid diffusivity. ES was developed based on the finding by Dawson et al. [43] that the ratio of the high- and low-pressure density-diffusivity products could be simplified as a polynomial of the mixture molar density. The low-pressure gaseous diffusion can be obtained from the kinetic theory of dilute gasses [44]. RW shares some similarity with ES, but it uses viscosity as a modeling parameter, inspired by the Stokes-Einstein theory. Among the five correlations, LDF is the only one explicitly using the MS framework. The correlation can estimate the MS diffusion coefficients as well as the generalized Fickian diffusion coefficients. LDF calculates the infinite dilution diffusion

coefficients first using a correlation like RW. The MS diffusion coefficients at other concentrations can then be estimated using the infinite dilution diffusion coefficients. Finally, the MS diffusion coefficients can be converted to Fickian coefficients with the help of a thermodynamic model.

In the following text, we will present Michelsen's method for CVD simulation, including the mathematical formulation of the CVD process and its numerical solution using the orthogonal collocation method. We will then briefly present the five diffusion coefficient correlations studied here. Finally, we will present the CVD simulation results based on Christoffersen's data [26]. In addition to the validation of the simulation and a discussion of the simulation strategy, we will present both prediction and regression results, as well as the profiles of diffusion coefficients. The aim of the study is two-fold. First, we will demonstrate the effectiveness of Michelsen's method in simulating CVD using constant or composition-dependent diffusion coefficients. Second, we will investigate the determination of diffusion coefficients from CVD tests and evaluate the impact of different treatments, such as the use of a constant diffusion coefficient or a composition-dependent coefficient calculated by one of the five correlations, on the results. Specifically, we will compare the five correlations in terms of their prediction and regression capabilities.

2. Mathematical model

Fig. 1 presents a schematic of the CVD test. The total height of the diffusion cell is *h*. The height of the liquid column is l(t), and that of the vapor column is h - l(t). There are N_c components in the system. If the convective flow is negligible, the diffusion equation can be written for each component *i*:

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x} \left(D_i \frac{\partial C_i}{\partial x} \right) = D_i \frac{\partial^2 C_i}{\partial x^2} + \frac{\partial D_i}{\partial x} \frac{\partial C_i}{\partial x}$$
(1)

In Eq. (1), *t* and *x* are dimensional time and distance, respectively, C_i is the molar concentration (mole per volume) of component *i*, and D_i is the effective diffusion coefficient of component *i* in a certain phase. The coefficient D_i is in principle concentration-dependent in each phase. In the case of constant D_i in each phase, the second term on the RHS of Eq. (1) disappears. However, even for this case, the diffusion coefficients in vapor (D_i^v) and liquid (D_i^l) still assume two different values. Eq. (1) holds for $i \in [1, N_c]$. For simplicity, we drop $i \in [1, N_c]$ in the equations in this paper.

The initial and boundary conditions are given by

$$t = 0: C_i^L = C_{i0}^L, C_i^V = C_{i0}^V, l = l_0$$
⁽²⁾

$$x = 0: \frac{\partial C_i^L}{\partial x} = 0 \tag{3}$$

$$x = l : f_i^L = f_i^V \tag{4}$$

$$x = h: \frac{\partial C_i^v}{\partial x} = 0 \tag{5}$$

At the initial state, the molar concentration of component *i* in vapor (C_i^V) and that in liquid (C_i^L) are uniform, equal to C_{i0}^V and C_{i0}^L , respectively. The initial height of the liquid column is l_0 . Eqs. (3) and (5) honor the fact that there is no transport at the upper and lower boundaries of the diffusion cell. Eq. (4) assumes instantaneous equilibrium at the vapor-liquid interface.

The overall mole balance for each component can be written as

$$n_i = \int_0^t C_i^L(x,t) dx + \int_l^n C_i^V(x,t) dx = l_0 C_{i0}^L + (h - l_0) C_{i0}^V$$
(6)

where n_i is the moles of component *i*.

Since the pressure gradient is small in the experiment, it is reason-

able to use an average pressure for each phase. The vapor phase pressure P^V and the liquid phase pressure P^L , calculated from their respective average concentrations \bar{C}^V and \bar{C}^L , should be equal to the system pressure P:

$$P^{L}\left(\bar{C}^{L},T\right) = P^{V}\left(\bar{C}^{V},T\right) = P \tag{7}$$

Eqs. (1)–(7) constitute a complete set of equations that can in principle be solved numerically to generate the molar concentration profiles at certain time. However, before proceeding to the numerical solution, it is advantageous to further transform and simplify the equations by introducing new variables.

During the CVD test, the vapor-liquid interface moves with time. To avoid continuous re-gridding during the numerical solution, it makes sense to define a new spatial variable χ :

$$\chi = \frac{x}{l(t)} \quad \text{for liquid} \tag{8}$$

$$\chi = \frac{h - x}{h - l(t)} \quad \text{for vapor} \tag{9}$$

The newly introduced spatial variable varies from 0 at the bottom boundary to 1 at the interface for the liquid, and from 0 at the top boundary to 1 at the interface for the vapor. The spatial coordinates therefore have opposite directions in the two phases. The diffusion equations given by Eq. (1) become two similar sets for liquid and vapor:

$$\frac{\partial C_i^L}{\partial t} = \frac{D_i^L}{l^2} \frac{\partial^2 C_i^L}{\partial \chi^2} + \frac{1}{l^2} \frac{\partial D_i^L}{\partial \chi} \frac{\partial C_i^L}{\partial \chi} + \frac{1}{l} \frac{dl}{dt} \chi \frac{\partial C_i^L}{\partial \chi} \quad \text{for liquid}$$
(10)

$$\frac{\partial C_i^V}{\partial t} = \frac{D_i^V}{(h-l)^2} \frac{\partial^2 C_i^V}{\partial \chi^2} + \frac{1}{(h-l)^2} \frac{\partial D_i^V}{\partial \chi} \frac{\partial C_i^V}{\partial \chi} - \frac{1}{h-l} \frac{dl}{dt} \chi \frac{\partial C_i^V}{\partial \chi} \quad \text{for vapor}$$
(11)

and the new boundary conditions are

$$t = 0: C_i^L = C_{i0}^L, C_i^V = C_{i0}^V, l = l_0$$
(12)

$$\chi = 0: \frac{\partial C_i^L}{\partial \chi} = 0, \frac{\partial C_i^V}{\partial \chi} = 0$$
(13)

$$\chi = 1: f_i^L = f_i^V \tag{14}$$

We further introduce $\eta = \chi^2$. With $\frac{\partial}{\partial \chi} = 2\sqrt{\eta} \frac{\partial}{\partial \eta}$, the boundary condition Eq. (13) is always satisfied and can be removed, leaving just one boundary condition

$$\eta = 1 : f_i^L = f_i^V \tag{15}$$

The resulting diffusion equations are

$$\frac{\partial C_{i}^{L}}{\partial t} = \frac{4\eta D_{i}^{L}}{l^{2}} \left(\frac{\partial^{2} C_{i}^{L}}{\partial \eta^{2}} \right) + \frac{2D_{i}^{L}}{l^{2}} \left(\frac{\partial C_{i}^{L}}{\partial \eta} \right) + \frac{4\eta}{l^{2}} \left(\frac{\partial D_{i}^{L}}{\partial \eta} \right) \left(\frac{\partial C_{i}^{L}}{\partial \eta} \right) + \frac{2\eta}{l} \left(\frac{dl}{dt} \right) \left(\frac{\partial C_{i}^{L}}{\partial \eta} \right)$$
for liquid (16)

assumed to be concentration independent, and the fourth terms disappear if the change of the interface level is negligible. In our study, we always include the fourth term to account for the varying interface height. The final set of equations consists of the diffusion Eqs. (16) and (17), the material balance equations Eq. (6), the pressure equality Eq. (7), the initial condition Eqs. (2) or (12), and the fugacity equalities at interface Eq. (15).

3. Numerical model

The equations formulated in Section 2 can be solved using the orthogonal collocation method. Eqs. (16) and (17) are discretized using a series of orthogonal collocation points. It can be shown that the concentrations on these collocation points, C_i^L and C_i^V , can be solved if the equilibrium concentrations at the interface, $C_i^{e,L}$ and $C_i^{e,V}$, and the liquid height l(t) are known. The final set of independent variables, $C_i^{e,L}$, $C_i^{e,V}$, $\lambda = l(t)/h$, and the system pressure *P*, should satisfy material balances, fugacity equalities, and the pressure equation for each phase.

3.1. Concentrations at the collocation points

We illustrate how to discretize Eq. (16) using the orthogonal collocation method and solve for C_i^L provided that $C_i^{e,L}$ and l(t) are known. The procedure for solving Eq. (17) is essentially the same. Here we drop the superscript L in Eq. (16) for simplicity. Also note that the solution procedure is the same for each component in the N_c components.

We select *N* interior collocation points η_m , which are the zeros of a suitable Jacobi polynomial $p_N^{(\alpha,\beta)}(\alpha = 0 \text{ and } \beta = -0.5 \text{ here})$. The first and second order derivatives of C_i w.r.t. η at $\eta = \eta_m$ can be expressed using the values $C_{i,n}$ at the *N* interior points and at $\eta = 1$:

$$\left(\frac{\partial C_{i,m}}{\partial \eta}\right)_{\eta=\eta_m} = \sum_{n=1}^{N+1} l_n^{(1)}(\eta_m) C_{i,n} = \sum_{n=1}^{N+1} A_{mn} C_{i,n}$$
(18)

$$\left(\frac{\partial^2 C_{i,m}}{\partial \eta^2}\right)_{\eta=\eta_m} = \sum_{n=1}^{N+1} l_n^{(2)}(\eta_m) C_{i,n} = \sum_{n=1}^{N+1} B_{mn} C_{i,n}$$
(19)

where $A_{mn} = l_n^{(1)}(\eta_m)$ and $B_{mn} = l_n^{(2)}(\eta_m)$ are the differentiation weights that can be generated after the collocation points are determined. These two derivatives can be evaluated implicitly using C_{i.n} at the current time step. If we use constant D_i , the spatial derivative of D_i is zero and the third term on the RHS of Eq. (16) disappears. However, in the general situation where composition-dependent D_i are used, we need to take into account the spatial variation of D_i and the third term on the RHS of Eq. (16). Since D_i is expected to vary with time slowly in the diffusion process, it is convenient to treat D_i in Eq. (16) and its derivative $\frac{\partial D_i}{\partial n}$ explicitly. That is, we calculate $D_{i,m}$ at the collocation point *m* using the concentrations from the old time step, C_{im}^{old} , and then evaluate its derivative using

$$D_{i,m}^{(1)} = \left(\frac{\partial D_{i,m}}{\partial \eta}\right)_{\eta = \eta_m} = \sum_{n=1}^{N+1} l_n^{(1)}(\eta_m) D_{i,n} = \sum_{n=1}^{N+1} A_{mn} D_{i,n}$$
(20)

$$\frac{\partial C_i^V}{\partial t} = \frac{4\eta D_i^V}{(h-l)^2} \left(\frac{\partial^2 C_i^V}{\partial \eta^2}\right) + \frac{2D_i^V}{(h-l)^2} \left(\frac{\partial C_i^V}{\partial \eta}\right) + \frac{4\eta}{(h-l)^2} \left(\frac{\partial D_i^V}{\partial \eta}\right) \left(\frac{\partial C_i^V}{\partial \eta}\right) - \frac{2\eta}{(h-l)} \left(\frac{dl}{dt}\right) \left(\frac{\partial C_i^V}{\partial \eta}\right)$$
for vapor

(17)

In the RHS of Eqs. (16) and (17), the third terms disappear if D is

Substitution of Eqs. (18)-(20) into Eq. (16) results in the collocation equations for the N interior points:

Table 1

An overview of the bina	y systems measured	by Christoffersen	[26].
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No.	Case ID	Vapor	Liquid	T (°C)	h _L (cm)	P ₀ (bar)	P _{final} (bar)	P _{eq} (bar)	Duration (hr)
1	C1-C5 M no.1	C_1	C ₅	21.4	22.60	94.9	73.5	54.1	161.9
2	C1-C5 M no.2	C1	C ₅	21.4	21.60	94.3	69.2	55.4	266.0
3	C1-C5 M no.3	C1	C ₅	24.0	18.20	96.7	72.2	64.1	328.1
4	C1-C8 M no.1	C1	C ₈	22.9	19.71	93.9	81.6	68.9	263.5
5	C1-C8 M no.2	C1	C ₈	21.6	20.20	95.8	83.9	69.4	225.3
6	C1-C8 M no.3	C1	C ₈	21.4	20.20	95.0	82.0	69.0	283.5
7	C1-C8 H no.1	C1	C ₈	23.6	19.33	177.2	153.9	133.3	308.0
8	C1-C8 H no.2	C1	C ₈	21.0	19.20	178.8	154.3	134.9	350.1
9	C1-C8 H no.3	C1	C ₈	21.5	19.40	183.7	156.9	138.2	400.3
10	C1-C10 M	C1	C10	21.4	20.90	97.1	87.0	73.5	310.3
11	C1-C10 H	C1	C10	21.5	20.20	180.5	165.2	142.5	258.8
12	C1-C16 M no.1	C1	C ₁₆	21.0	22.80	95.6	90.6	77.1	250.3
13	C1-C16 M no.2	C1	C ₁₆	21.0	22.50	95.8	89.5	77.3	404.3
14	C1-C16 H no.1	C1	C ₁₆	25.7	17.70	179.6	173.3	158.8	271.2
15	C1-C16 H no.2	C1	C16	25.8	17.66	184.6	177.4	163.0	308.6
16	N2-C5 M no.1	N_2	C ₅	21.0	17.28	98.5	90.9	86.7	235.3
17	N2-C5 M no.2	N_2	C ₅	23.6	19.20	100.1	92.1	86.0	207.1
18	N2-C5 H no.1	N_2	C ₅	23.7	18.42	178.8	165.7	156.7	234.4
19	N2-C5 H no.2	N_2	C ₅	21.5	17.90	181.8	168.3	159.1	239.8
20	N2-C8 M	N_2	C ₈	22.0	19.80	98.7	94.0	89.6	332.0
21	N2-C8 H	N_2	C ₈	20.8	19.70	179.4	173.7	165.0	235.5
22	N2-C10 M	N_2	C10	20.5	20.10	97.2	94.1	89.8	312.9
23	N2-C10 H	N_2	C10	21.2	20.00	184.6	180.3	172.3	233.6
24	N2-C16 M no.1	N_2	C ₁₆	21.5	22.10	93.6	92.7	88.0	90.3
25	N2-C16 M no.2	N ₂	C ₁₆	21.5	22.10	95.4	94.7	89.8	67.3
26	N2-C16 H	N_2	C ₁₆	25.7	17.64	177.8	174.9	171.0	529.8

Table 2

Parameters used for the SRK EoS and the diffusion coefficient models.

Component	T _C (K)	P _C (bar)	Acentric factor	\$ _{SHIFT}	MW (g/mol)	V _C (cm ³ /mol)	V _A (cm ³ /mol)	$\sum v_i$
N ₂	126.3	33.99	0.0358	0.085	28.01	90.09	34.753	18.50
C1	190.6	46.04	0.0074	0.100	16.04	99.27	37.984	25.14
C ₅	469.6	33.69	0.2522	0.104	72.15	303.99	118.330	107.22
C ₈	568.8	24.86	0.3998	0.160	114.23	492.14	186.58	168.78
C ₁₀	617.6	20.96	0.4916	0.200	142.29	603.17	235.61	209.82
C ₁₆	720.5	14.20	0.7667	0.268	226.43	953.43	373.78	332.94

Table 3

Non-zero binary interaction coefficients (BIC) for SRK.

Binary pair	BIC
N ₂ -C ₅	0.150
N2-C8	0.200
N ₂ -C ₁₀	0.250
N ₂ -C ₁₆	0.320
C1-C5	0.032
C1-C8	0.060
C1-C10	0.070
C1-C16	0.100

$$\begin{pmatrix} C_{i,m} - C_{i,m}^{old} \end{pmatrix} - \frac{\Delta t}{l^2} \sum_{n=1}^{N+1} \left(4\eta_m D_{i,m} B_{nn} + 4\eta_m D_{i,m}^{(1)} A_{mn} + 2D_{i,m} A_{mn} \right) C_{i,n}$$

- $\frac{l - l^{old}}{l} \sum_{n=1}^{N+1} 2\eta_m A_{mn} C_{i,n}$
= 0 (21)

Note that $C_{i,N+1}$ is essentially the equilibrium concentration at the interface $C_i^{e,L}$. We can write Eq. (21) in a matrix-vector form:

$$\mathbf{E}\mathbf{c}_i = \mathbf{q} \tag{22}$$

with

$$\mathbf{c}_{i} = \left(C_{i,1}, C_{i,2}, ..., C_{i,N}\right)^{T}$$
(23)



Fig. 2. The pressure curves from the CVD simulator and E300 for C_1 - C_{10} M.



Fig. 3. The relative changes in BIC and D_L after matching the equilibrium pressure.



Fig. 4. Influence of tuning BIC on the pressure curve (a) C1-C5 M no.3 (b) C1-C16 M no.2.

$$E_{mn} = \delta_{mn} - \frac{\Delta t}{l^2} \left(4\eta_m D_{i,m} B_{mn} + 4\eta_m D_{i,m}^{(1)} A_{mn} + 2D_{i,m} A_{mn} \right) - \frac{l - l^{old}}{l} 2\eta_m A_{mn}$$

$$(24)$$

$$q_m = C_{i,m}^{old} + \frac{\Delta t}{l^2} \left(4\eta_m D_{i,m} B_{m,N+1} + 4\eta_m D_{i,m}^{(1)} A_{m,N+1} + 2D_{i,m} A_{m,N+1} \right) C_i^{e,L}$$

$$+ \frac{l - l^{old}}{l} 2\eta_m A_{m,N+1} C_i^{e,L}$$

$$(25)$$

From Eq. (22), we can solve $C_{i,n}$ at the *N* collocation points. From $C_{i,n}$, we can readily calculate the average concentration \overline{C}_i using the Gaussian quadrature. Eq. (22) can be further used to evaluate $\frac{de_i}{dC_i^{cL}}$ and $\frac{de_i}{dl}$, and we

only need to change its RHS to $\mathbf{q}_{l}^{C_{l}^{e,L}}$ and \mathbf{q}^{l} , respectively:

$$\begin{aligned} q_{m}^{c_{i}^{c,L}} &= \frac{\Delta t}{l^{2}} \left(4\eta_{m} D_{i,m} B_{m,N+1} + 4\eta_{m} D_{i,m}^{(1)} A_{m,N+1} + 2D_{i,m} A_{m,N+1} \right) \\ &+ \frac{l - l^{old}}{l} 2\eta_{m} A_{m,N+1} \end{aligned}$$
(26)

$$q_{m}^{l} = \sum_{n=1}^{N+1} \left\{ \left[-2\frac{\Delta t}{l^{3}} \left(4\eta_{m} D_{i,m} B_{nm} + 4\eta_{m} D_{i,m}^{(1)} A_{mn} + 2D_{i,m} A_{mn} \right) + \frac{l^{old}}{l^{2}} 2\eta_{m} A_{m,n} \right] C_{i,n} \right\}$$
(27)

The derivatives of the average concentration, $\frac{\partial \hat{C}_i}{\partial C_i^{eL}}$ and $\frac{\partial \hat{C}_i}{\partial l}$, can also be evaluated using the Gaussian quadrature.

3.2. Solution for $C_i^{e,L}$, $C_i^{e,V}$, λ , and P

For two-phase diffusion with N_C components, the $2N_C + 2$ variables, $C_1^{e,L}, \ldots, C_{N_c}^{e,L}, C_1^{e,V}, \ldots, C_{N_c}^{e,V}, \lambda = l/h$, and P, must satisfy the following $2N_C + 2$ equations

$$f_i = \lambda \overline{C}_i^L + (1 - \lambda) \overline{C}_i^V - \overline{C}_i^0 = 0, \quad i = 1, \dots N_C$$
(28)

$$f_{N_{C}+i} = \phi_i^{e,L} x_i^e - \phi_i^{e,V} y_i^e = 0, \quad i = 1, ..., N_C$$
⁽²⁹⁾

$$f_{2N_{C}+1} = \frac{P}{Z_{x}T} - \sum_{k=1}^{N_{C}} \bar{C}_{k}^{L} = 0$$
(30)

$$f_{2N_C+2} = \frac{P}{Z_y T} - \sum_{k=1}^{N_C} \bar{C}_k^V = 0$$
(31)

These equations are from Eqs. (6), (7) and (15). Note that x_i^e and y_i^e in Eq. (29) are the equilibrium liquid and vapor mole fractions at the interface:

$$x_{i}^{e} = \frac{C_{i}^{e,L}}{\sum_{k=1}^{N_{C}} C_{k}^{e,L}}$$
(32)

$$y_{i}^{e} = \frac{C_{i}^{e,V}}{\sum_{k=1}^{N_{c}} C_{k}^{e,V}}$$
(33)

 $\phi_i^{e,L}$ and $\phi_i^{e,V}$ are the fugacity coefficients corresponding to x_i^e and y_i^e , respectively. In Eqs. (30) and (31), Z_x and Z_y are the compressibility factors corresponding to the overall compositions \bar{C}_i^L and \bar{C}_i^V at the average system pressure P.

The Jacobian for Eqs. (28)-(31), obtained by differentiating $f_i(i=1,...,2N_C+2)$ w.r.t. $(C_1^{e,L},...,C_{N_c}^{e,L},C_1^{e,V},...,C_{N_c}^{e,V},\lambda,P)$, assumes the following form:



where "×" marks the non-zero elements. Appendix A provides detailed expressions for the Jacobian.

3.3. Solution procedure

A solution procedure can be developed based on the details given in Sections 3.1 and 3.2. It consists in the solution of the $2N_C + 2$ variables $(C_i^{e,L}, C_i^{e,V}, l, and P)$ using Newton's method and the solution of the $2N_C$ diffusion Eqs. (16) and (17) using the orthogonal collocation method. In the solution of the diffusion equations, implicit treatment is used for all the spatial derivatives of C_i and explicit treatment is used for all the D_i terms. The procedure is summarized below:

1 Set the initial conditions according Eq. (12). 2 Set initial estimates $C_i^{e,L} = C_i^{0,L}$, $C_i^{e,V} = C_i^{0,V}$, $l = l^0$, and $P = P^0$. If there are only two components, one can in principle solve the twophase equilibrium at T and P to obtain the equilibrium compositions as initial estimates for $C_i^{e,L}$ and $C_i^{e,V}$.

- 3 Advance time by Δt .
- 4 Estimate $D_{i,m}$ and $D_{i,m}^{(1)}$ using $C_{i,m}^{old}$ for both liquid and gas phases.
- 5 Solve Eq. (22) for $C_{i,m}$ and evaluate the average concentrations \overline{C}_i and their sensitivities w.r.t. C_i^e and l. Repeat the calculation for all the components in both phases.
- 6 Update $C_i^{e,L}$, $C_i^{e,V}$, l, and P using Newton's method for Eqs. (28) and
- 7 If the updates in step 6 are higher than the tolerance, go back to step 5. Otherwise, the Newton method has converged, and we proceed to the next time step by going to step 3. The loop from step 3 to step 7 terminates if the final simulation time is reached.

It is worthwhile to note that this algorithm is not restricted to the initial condition of uniform concentrations in both phases. But for CVD processes, it is usually the case.

The above CVD algorithm uses the orthogonal collocation method. It should be noted that the mathematical treatment in Section 2 and the thermodynamic treatment in Section 3 can also be applied to the finite difference or finite volume methods. The advantage of the orthogonal collocation method is that it achieves the same accuracy with a much smaller set of equations than the finite difference or finite volume methods

4. Diffusion coefficient models

A brief review of the five diffusion coefficient correlations studied here, including WC, HM, ES, RW, and LDF, is provided here to summarize the major equations, model parameters, and other correlations involved in the estimation of diffusion coefficients.

4.1. Wilke-Chang (WC) correlation

The WC correlation (1955), originally designed for lowconcentration solute A in solvent B, is an empirical modification of the Stokes-Einstein relation:

$$D_{AB}^{o} = \frac{7.4 \times 10^{-8} (\Phi M_B)^{1/2} T}{\eta_B V_A^{0.6}}$$
(35)

where D_{AB}^o is the mutual diffusion coefficient (cm²/s) of solute A at very low concentrations in solvent B, M_B is the molecular weight (g/mol) of solvent B, T is temperature (K), η_B is the viscosity (cP) of solvent B, V_A is the molar volume (cm^3/mol) of solute A at its normal boiling temperature, and Φ is the association factor (dimensionless) of solvent *B*. For the non-associating solvents studied here, Φ is always equal to unity. WC is designed for dilute solutions. For a non-dilute solution, there is no consensus on how to interpret η_B and M_B . One convenient solution is to treat them as the properties of the solution instead of the solvent B. However, there is an ambiguity regarding the choice of solute/solvent component, leading to inconsistency when the role of solute and that of solvent are swapped.

4.2. Hayduk–Minhas (HM) correlation

Hayduk and Minhas proposed a set of correlations for liquid diffusivities similar to WC in 1982. The proposed correlations are in principle only applicable to the infinite dilution binary diffusion coefficients. The following correlation was developed based on normal paraffin solutions and generally recommended for hydrocarbons:

$$D_{AB}^{o} = \frac{13.3 \times 10^{-8} T^{1.47} \eta_{B}^{\left(\frac{10.2}{V_{A}} - 0.791\right)}}{V_{A}^{0.71}}$$
(36)







Fig. 6. Predicted CVD pressure curves for C_1 - C_X^7 systems with the initial pressure around 95 bar.



Fig. 7. The predicted CVD pressure curves by different models for C1-Cx systems with the initial pressure between 150 and 180 bar.

The symbols in the above equation have the same meaning as in WC. Compared to WC, HM does not require M_B . It has the same inconsistency problem as WC.

4.3. Extended Sigmund (ES) correlation

Sigmund developed in 1976 a correlation for the binary diffusion coefficients D_{ij} based on the corresponding states principle. He expressed the ratio of molar density-diffusivity product, $\rho_M D_{ij} / \rho_M^o D_{ij}^o$, as a polynomial in the pseudo-reduced molar density ρ_{Dr} :

$$\frac{\rho_M D_{ij}}{\rho_M^o D_{ij}^o} = 0.99589 + 0.096016\rho_{pr} - 0.22035\rho_{pr}^2 + 0.032874\rho_{pr}^3 \tag{37}$$

In the equation, the molar density ρ_M (mol/cm³) and the binary diffusion coefficient D_{ij} (cm²/s) are at the system temperature and pressure. ρ_{pr} is calculated as $\frac{\rho_M}{\rho_c}$, where ρ_c is the mixture pseudo-critical molar density (mol/cm³), given by

$$\rho_c = \frac{\sum x_i v_{ci}^{2/3}}{\sum x_i v_{ci}^{5/3}}$$
(38)

with v_{ci} being the critical molar volume (cm³/mol) and x_i being the mole fraction of component *i*. The low-pressure density-diffusivity product $\rho_M^o D_{ij}^o$ is a function of temperature and composition only, and can be calculated using the Chapman-Enskog dilute gas theory [44,45]. Da Silva and Belery, in 1989, devised a small modification of the Sigmund correlation. They noticed that Eq. (37) provides negative diffusion coefficients at high ρ_{pr} and thus suggested using the equation only for $\rho_{pr} \leq 3$. For $\rho_{pr} > 3$, they proposed the following modification:

$$\frac{\rho_M D_{ij}}{\rho_M^o D_{ij}^o} = 0.18839 \exp\left(3 - \rho_{pr}\right) \tag{39}$$

Eq. (37) together with Eq. (39) are known as the extended Sigmund (ES) correlation.



Fig. 8. The predicted CVD pressure curves by different models for N₂-C_X systems with the initial pressure between 90 and 100 bar.

4.4. Riazi-Whitson (RW) correlation

Riazi and Whitson in 1993 developed a correlation to estimate diffusion coefficients of dense gasses and liquids for both binary and multicomponent systems. Its development was inspired by both the hydrodynamic theory (using viscosity) [41] and the kinetic theory of gasses (using density) [20]. The correlation for a binary mixture is given by:

$$\frac{\rho_M D_{AB}}{\rho_M^o D_{AB}^o} = a \left(\frac{\mu}{\mu^o}\right)^{b+cP_r} \tag{40}$$

where $\rho_M D_{AB}$ and $\rho_M^o D_{AB}^o$ are the density-diffusivity product at the system conditions and at the low-pressure, respectively. The molar density ρ_M is in mol/cm³ and the binary diffusion coefficient D_{AB} is in cm²/s. As in ES, $\rho_M^o D_{AB}^o$ is calculated from the Chapman-Enskog dilute gas theory. The coefficients *a*, *b*, and *c* in Eq. (40) are given by a = 1.07, $b = -0.27 - 0.38\omega$, and $c = -0.05 + 0.1\omega$. The reduced pressure P_r is calculated by $P_r = P/P_c$. The mixture critical pressure P_c and acentric factor ω are calculated using mole fraction-based linear mixing rules. The low-pressure mixture viscosity μ^0 is estimated from the Stiel and Thodos correlation [46], with the viscosity at the system conditions μ from the generalized Jossi-Stiel-Thodos (1962) correlation [47], which is essentially the same as the so-called Lohrenz-Bray-Clark (LBC) correlation [48] in the petroleum industry.

4.5. Leahy-Dios and Firoozabadi (LDF) correlation

The LDF correlation proposed in 2007 uses the MS framework explicitly. In this approach, the infinite dilution diffusion coefficients are estimated first using the following correlation:

$$\frac{cD_{21}^{\infty}}{(cD)^{0}} = A_0 \left(\frac{T_{r,1}P_{r,2}}{T_{r,2}P_{r,1}}\right)^{A_1} \left(\frac{\mu}{\mu^0}\right)^{[A_2(\omega_1,\omega_2) + A_3(P_r,T_r)]}$$
(41)

The correlation bears some similarities to ES and RW, especially the



Fig. 9. The predicted CVD pressure curves by different models for N₂-C_X systems with the initial pressure around 180 bar.

latter. The ratio of the density-diffusivity product $\frac{cD_{21}^{\infty}}{(cD)^0}$ is expressed as a function of the viscosity ratio $\frac{\mu}{\mu^0}$, reduced temperatures $T_{r,i}$ pressures $P_{r,i}$, and acentric factors ω_i . Different from ES and RW, the molar density c and the viscosity μ are for the solvent component 1 instead of the mixture at the system temperature and pressure, and D_{21}^{∞} is the infinite-dilution diffusion coefficient of component 2 in component 1 instead of the D at the given composition. $(cD)^0$ is the dilute gas density-diffusivity product, which can in principle be calculated by the Chapman-Enskog dilute gas theory as in ES and RW, but Leahy-Dios and Firoozabadi suggested using the approach of Fuller et al. [49]:

$$(cD)^{o} = 1.01 \times 10^{-2} T^{0.75} \frac{\left(\frac{1}{M_{1}} + \frac{1}{M_{2}}\right)^{0.5}}{R\left[\left(\sum v_{1}\right)^{1/3} + \left(\sum v_{2}\right)^{1/3}\right]^{2}}$$
(42)

where M_1 and M_2 are the molar masses (g/mol) of components 1 and 2, respectively. $\sum v_i$ is the so-called "diffusion volume increments" of

component *i*, and can be calculated by summing the atomic diffusion volumes [50]. The dilute gas viscosity μ^0 is calculated by the Stiel and Thodos correlation [46] evaluated at the equimolar composition of components 1 and 2. Leahy-Dios and Firoozabadi did not suggest a single-set of models for *c* and μ . In their original development of Eq. (41), they used experimental data whenever available; for hydrocarbons, they used the corresponding states theory [51] for μ , and PR-EoS with volume translation for *c*.

Once the infinite-dilution diffusion coefficients for each pair of the components in the *n*-component mixture, D_{ij}^{∞} , are estimated, we can estimate the MS diffusion coefficients D_{ij} at the desired composition using the generalized Vignes relation:

$$\mathcal{D}_{ij} = \left(D_{ij}^{\infty}\right)^{x_j} \left(D_{ji}^{\infty}\right)^{x_i} \prod_{\substack{k=1\\k\neq i,j}}^{n} \left(D_{ik}^{\infty} D_{jk}^{\infty}\right)^{x_k/2} \qquad i, j = 1, ..., n, i \neq j$$
(43)

Table 4

Summary of the features of the D_L correlations.

Model	Features	Remark
ES	Overpredicts the pressure for C ₁ - C _x ; acceptable prediction for N ₂ -C _x . Large variations in the regressed D_L range for gas in heavier n-alkanes (C ₁ in C ₈ /C ₁₀ /C ₁₆ and N ₂ in C ₁₀ / C ₁₆) whereas small variations in lighter n-alkanes (C ₁ / N ₂ in C ₅) D_L decreases toward the interface, the opposite to the others' trends in general.	• The abnormal <i>D</i> _L trend is caused by the strong dependence on the molar density and critical density.
RW	Similar prediction to WC/HM for C_1 - C_x at 95 bar but poorer at 150–180 bar; inferior to WC/HM in prediction for N ₂ - C_x . D_L increases toward the interface in most cases but slightly decreases for some cases (heavier n-alkanes at a higher pressure).	 Besides solution viscosity, other factors also play a role. A hybrid of the ES approach and the WC/HM one; LDF adopts a similar but more complex form.
LDF	Significantly underpredicts the pressure for C_1 - C_x ; acceptable prediction for N_2 - C_x . D_L increases toward the interface.	The generalized Vignes relation might be inadequate to estimate diffusivity for gas-liquid systems.
WC/ HM	Overall the best prediction for C ₁ - C _x and N ₂ -C _x . $D_{\rm L}$ increases toward the interface.	Solution viscosity plays a major role.Note the ambiguity in defining solute and solvent.

$$B_{ij}^{M} = -x_i \left(\frac{1}{D_{ij}} - \frac{1}{D_{in}} \right), \quad i, j = 1, \dots, n-1, i \neq j$$
(46)

The Γ matrix contains the following thermodynamic factors (dimensionless):

$$\Gamma_{ij} = x_i \left(\frac{\partial \ln f_i}{\partial x_j}\right)_{x_{k \neq j,n}, T, P}, \quad i, j = 1, \dots, n-1$$
(47)

where f_i is the fugacity of component i. The Γ matrix represents the fluid mixture non-ideality at the given conditions and can be calculated using an activity coefficient model or equation of state. For a binary mixture, the Γ matrix has only one element:

$$\Gamma_{11} = x_1 \left(\frac{\partial \ln f_1}{\partial x_1}\right)_{T,P} \tag{48}$$

and the only Fickian diffusion coefficient is given by

$$D_{11}^{M} = D_{12}\Gamma_{11} \tag{49}$$

5. Results and discussions

5.1. CVD measurements by Christoffersen

We used the CVD simulator to simulate a series of CVD tests for binary mixtures (methane/nitrogen with various n-alkanes) measured by Christoffersen [26]. Christoffersen reported 26 CVD experiments [26] for eight binary systems: C1-C5, C1-C8, C1-C10, C1-C16, N2-C5, N2-C8, N_2 - C_{10} , and N_2 - C_{16} at around 22 °C and 90 – 180 bar. The measurement conditions are collected in Table 1. Christoffersen's tests were conducted at two pressure levels, around 90 and 180 bar. We use M and H in the case ID to represent the two pressure levels, respectively. All the CVD measurements were performed in a Ruska high-pressure visual cell with a height of 49.0 cm. In the experiment, the cell was evacuated first and then filled with a given amount of liquid. After a brief evacuation to remove air, gas was injected from the top, marking the start of the measurement. The initial pressure P₀ and the initial liquid height h_L are provided in Table 1. Ratnakar and Dindoruk [28] recently discussed the minimum time criteria for CVD tests when using an analytical approach in data processing. Christoffersen did not discuss this specifically, but his measurements lasted quite a long time, typically over 10 days. The



Fig. 10. Regression results by different models for C1-C5 M no.2.

This equation utilizes the fact that at the infinite dilution limit, all molecular diffusion coefficients become equal.

Finally, the MS diffusion coefficients can be converted to the molebased generalized Fickian diffusion coefficients D_{ij}^{M} with the following transformation:

$$\boldsymbol{D}^{M} = \left[\boldsymbol{B}^{M}\right]^{-1} \boldsymbol{\Gamma}$$
(44)

Here D^M is the (*n*-1)-dimension square matrix of mole-based Fickian diffusion coefficients, and the transformation matrix B^M is given by

$$B_{ii}^{M} = \frac{x_{i}}{D_{in}} + \sum_{\substack{k=1\\i\neq k}}^{n} \frac{x_{k}}{D_{ik}}, \quad i = 1, ..., n - 1$$
(45)



Fig. 11. Fitted D_L using different diffusion coefficient correlations.

pressure variation with time was recorded for all the tests and the liquid height variation with time for some tests. P_{final} in Table 1 is the pressure at the end of each measurement. The cell was then rocked to equilibrate the system and determine the equilibrium pressure P_{eq} . Christoffersen reported 0.5 bar in accuracy and 0.06 bar in resolution for the pressure transducer, and 0.2 K in accuracy and 0.01 K in resolution for the temperature one. The resolution of the liquid level is 0.001 cm. Some systems in Table 1 have duplicate or triplicate measurements although their initial pressures are not exactly the same.

The SRK EoS parameters suggested by Christoffersen [26], including critical temperatures, critical pressures, acentric factors, volume shift parameters (s_{SHIFT}), and non-zero binary interaction coefficients (BIC), are provided in Table 2 and Table 3. It should be noted that the parameters in Table 2 are kept constant in our modeling here whereas the BIC in Table 3 may be tuned. Table 2 also provides other parameters needed for calculating viscosity and diffusion coefficients. The molar volume V_A of solute A at its normal boiling temperature is required by WC and HM. It is estimated from the NIST data whenever possible. If not available (only for C₁₆ here), it is estimated by the Tyn and Calus correlation [52]. LDF requires the so-called "diffusion volume increments" $\sum v_i$ in its dilute gas diffusivity calculation by the approach of Fuller et al. [49]. $\sum v_i$ is calculated by summing the atomic diffusion volumes [50,53].

5.2. Validation of the CVD simulator

We compared the CVD simulator with the commercial reservoir simulator Eclipse 300 (E300) for three cases (C1-C5 M no.1, C1-C10 M, C1-C₁₆ H no.2) in Christoffersen's measurements as validation. The same simulation and model parameters were used in both simulators, including the tube length, the initial pressure, the interface height, and the SRK parameters from Tables 1 and 2. The CVD simulator used 8 collocation points for both liquid and gas regions. In the finite difference E300 simulation, 500 grid blocks were used. The orthogonal collocation approach results in a much smaller system of equations to solve. Since E300 only supports constant diffusion coefficients, we chose to use constant diffusion coefficients in our simulator. Fig. 2 shows the curves simulated from two simulators for C1-C10 M and the figures for the other two cases are provided in Supplementary Material. With the same diffusion coefficients, the two simulators produce almost the same curves not just in the measurement period but also in the extended simulation period till equilibrium. It should also be noted that E300 also solves a pressure equation and has a convective flow term. Obviously,

neglecting these in the CVD simulator does not lead to any significant difference. The comparison has validated the accuracy and reliability of the CVD simulator.

5.3. Default setting for CVD simulation

In the CVD simulation, different options can be selected regarding the gas-phase diffusion coefficient, the BIC, and the objective function used for regression (pressures only or both pressures and liquid heights). We performed a series of sensitivity analyses to evaluate the influence of different parameters/options on the simulation results, based on which we define the default parameter settings. For simplicity, the analyses in this subsection were made using constant diffusion coefficients.

5.3.1. Influence of gas-phase diffusion coefficients

For all 26 systems, we compared two strategies: tuning both liquidphase (D_L) and gas-phase diffusion coefficients (D_G) and tuning only D_L but keeping D_G constant (equal to a middle value of the range estimated by ES). The detailed results are provided in Supplementary Material. It turns out the maximum change in the fitted D_L is 0.164 cm²/day (C_1 - C_8 H no.3), which represents a relative change of 2.7%. It is also shown in Supplementary Material that both fitting options give nearly the same pressure curve. Another case N_2 - C_5 H no.1, corresponding to the largest D_G difference (17.21 cm²/day) in the regression results, is also illustrated in the Supplementary Material. The calculated pressure curves from both regression options are nearly indistinguishable. The comparison shows that the fitted D_L is insensitive to D_G and it is reasonable to use a D_G estimated from ES. It also shows that CVD is not a test suitable for determining D_G .

5.3.2. Tuning BIC to match the equilibrium pressure

The determination of D_L is directly related to the phase equilibrium modeling using the volume-translated SRK EoS. The model should accurately reproduce the final equilibrium pressure, which can be achieved by tuning the BIC between the gas component and the solvent. For all 26 cases, the relative change of BIC (Eq. (50)) and relative change of D_L (Eq. (51)) for the 26 tested cases are shown in Fig. 3. The figure reveals that non-negligible tunings are needed for many systems and the impact on D_L is significant for most cases. For cases like C_1 - C_5 M no.3 and C_1 - C_{16} M no.2, the relative change in D_L can reach around 30%. It is interesting to note a positive correlation between the change in BIC and the change in D_L . This is because a larger BIC gives a smaller gas solubility, which requires a larger diffusion coefficient to reach the same



Fig. 12. The diffusion coefficients (blue to red solid lines) and molar concentration (green to yellow dash lines) of C_1 in C_5 within the first 24 h by different models for C_1 - C_5 M no.1. The dotted line represents the fitted constant D_L .

magnitude of pressure decay.

BIC relative change =
$$\frac{(BIC^{uned} - BIC^{original})}{BIC^{original}}$$
 (50)

$$D_L \text{ relative change} = \frac{\left(D_L^{timed} - D_L^{original}\right)}{D_L^{original}}$$
(51)

Fig. 4 shows the pressure curves with and without matching the equilibrium pressure for two selected cases. Fig. 4(a) is a case where a slight increase of BIC is needed, resulting a slightly higher D_L to match pressure decay data. The original BIC also gives a good match but undershoots the equilibrium pressure. Fig. 4(b) is a case where the tuning becomes really critical. The original BIC fits the data but significantly overpredicts the equilibrium pressure. The correct D_L determined with the tuned BIC is much smaller than the one determined by the original BIC. Tuning BIC to match the equilibrium pressure is crucial to the

determination of the correct D_L. In engineering applications, the "optimal" BIC is often determined by matching different equilibrium data and it is generally desired to have a single optimal BIC value. In those situations, we may have to accept a BIC different from the one used in determining D_L. We should bear in mind that the pressure decay curve is determined by D_L and BIC together, and make sensible adjustments of D_L if the pressure decay behavior is to be modeled.

5.3.3. Pressure and liquid height in the objective function

The pressure variation is easily available from CVD but the liquid height variation is not always reported. Only 13 cases in Christoffersen's data have the liquid height data. We can set objective functions to include (1) only pressure, (2) both pressure and liquid height with 50% weight for each, or (3) only liquid height. The regressed D_L corresponding to three options, as shown in Fig. 5, are similar in general. The maximum D_L difference between (1) and (3) is $1.94 \text{ cm}^2/\text{day}$ for N₂-C₁₀ H. On average, the relative deviation between (1) and (3) is 12.4%. The



Fig. 13. The diffusion coefficients (blue to red solid line) and molar concentration (green to yellow dash line) of C_1 in C_5 until 422 h by different models for C_1 - C_5 M no.1. The dotted line represents the fitted constant D_L .

option (2) tends to give a D_L in the middle. Although it may be preferable to use both pressure and height data when they are available, the height data are not always available, and their accuracy is often not as good as the pressure data. It is considered reasonable to use the pressure data only, as we will practice in the subsequent discussions.

5.3.4. Default setting

The above analysis leads to the following default setting in our subsequent CVD simulations: We fit D_L only and estimate D_G by ES or LDF (LDF used for the LDF correlation and ES for the others); We adjust the BIC in the PVT model (SRK with volume translation) to match the measured equilibrium pressure before the CVD simulation; We only include pressure in the objective function.

5.4. Predictive calculation

The predicted pressure curves using different diffusion coefficient

correlations are compared with the measured data to investigate the predictivity of these correlations. The comparison can reveal some general trends of these correlations in predicting the diffusion in C_1 - C_x and N_2 - C_x systems. It is impossible to illustrate the results for all 26 systems. We selected some representative cases in Fig. 6 to Fig. 9 to cover the two types of systems at two pressure levels.

Fig. 6 shows the prediction results for C_1 - C_5 , C_1 - C_8 , C_1 - C_{10} and C_1 - C_{16} systems at around 95 bar. LDF generally underestimates the pressure and gives the largest deviations. ES overestimates the pressure for C_1 - C_5 , C_1 - C_8 , and C_1 - C_{10} , with the overestimation decreasing for a heavier solvent. ES slightly underestimates the pressure for C_1 - C_{16} . The predictions by RW, WC, and HM are similar and close to the experimental data. Fig. 7 shows the results at an initial pressure around 150 bar, which have similar general characteristics to Fig. 6. Nevertheless, two differences are worth mentioning here: (1) ES overestimates the pressure significantly for C_1 - C_5 and C_1 - C_8 , and the extents are larger than the underestimations by LDF for these two systems. It seems that the



Fig. 14. The diffusion coefficients (blue to red solid line) and molar concentration (green to yellow dash line) of C_1 in C_5 until equilibrium state by different models for C_1 - C_5 M no.1. The dotted line represents the fitted constant D_L .

performance of ES becomes worse at a higher pressure. (2) RW is no longer similar to WC and HM, and its deviation becomes larger.

Fig. 8 shows the results for the N₂-C_X systems at an initial pressure around 95 bar. Compared to C₁-C_X with initial pressures around 100 bar in Fig. 6, all the models give a much smaller deviation in Fig. 8. Generally, D_L is better predicted for N₂-C_X than C₁-C_X. LDF still gives an underestimation, and WC and HM predict satisfactorily for C₅/C₈/C₁₀. ES gives an overestimation for N₂-C₅ but an underestimation for the heavier system N₂-C₁₀. RW performs similarly to ES here. For N₂-C_X at an initial pressure around 180 bar (Fig. 9), the pressure decay is much weaker than that at a lower pressure (Fig. 8) and that for C₁-C_X systems (Figs. 6 and 7). In general, the pressure estimation errors by all the five correlations are within one bar. WC and HM again provide satisfactory prediction here.

Table 4 summarizes the main features of these correlations observed in this section and in Sections 5.5 and 5.6. We group WC and HM together due to their similarity. Not all the observed features can be attributed to a definite cause, and we just provide some relevant remarks for each model. LDF seems to have a problem in predicting the D_L in C_1 - C_x mixtures. We also noticed that LDF performed poorly for the D_L in gas-liquid mixtures in a recent publication [24]. This is probably caused by the generalized Vignes' relation (Eq. (43)) used in calculating the diffusion coefficient in a mixture from the diffusion coefficients of the corresponding infinite dilute solutions. In the case of a gas-liquid mixture like C_1 and C_x , the infinite dilute solution of C_x in C_1 may not be an adequate reference since its physical state may be more gas-like. Furthermore, for a gas at a temperature lower than its critical temperature, one may find two infinite dilute solutions and must decide which one to choose. For C_1 - C_x with a substantial C_1 solubility in the liquid phase, this problem appears more severe. For N_2 - C_x with a much smaller gas solubility, the problem is less obvious.



Fig. 15. The diffusion coefficients (blue to red solid line) and molar concentration (green to yellow dash line) of C_1 in C_{10} within first 400 h by different models for C_1 - C_{10} M. The dotted line represents the fitted constant D_L .

5.5. Regression calculation

Regression of D_L was performed using constant D_L and compositiondependent D_L . For composition-dependent D_L , a multiplication factor was applied to the D_L calculated by one of the five correlations. It can be shown that using constant D_L or the D_L correlations give essentially comparable regression results. Even for the case with the largest deviation (C_1 - C_5 M no.2), the difference is hardly noticeable (smaller than 0.2 bar), as shown in Fig. 10. More details about the regression deviations can be found in Supplementary Material. It indicates that all these regression options are sufficiently flexible to capture the measured pressure decay trends.

Fig. 11 shows the regressed D_L for all 26 systems. When a D_L correlation is used, the obtained D_L varies in a range. The constant D_L values are marked as black points in the figure.

For C₁-C_x, ES gives the smallest variation range for the lightest C₁-C₅,

but generally the largest variations for C_1 - C_8 , C_1 - C_{10} and C_1 - C_{16} . The largest variation (around 9.8 cm²/day) appears in C_1 - C_{10} H. For ES, the molar fraction does not explicitly appear in Eqs. (37) and (39). Instead, the composition dependence is through the calculated molar density. Similarly, WC and HM do not have an explicit dependence on the mole fraction in Eqs. (35) and (36). However, the viscosity term in WC and HM is mole fraction dependent. The diffusion coefficient variation is the smallest for the C_1 - C_{16} systems for WC and HM.

ES and WC/HM represent two different types of correlations, the former molar density-based and the latter viscosity-based. Nevertheless, both ES and WC/HM seem to give a larger D_L variation at a higher pressure, e.g., C_1 - C_{10} for ES and C_1 - C_8 , C_1 - C_{10} , and C_1 - C_{16} for WC/HM. The magnitudes of variation are different for two types: ES shows smaller variations for C_1 - C_5 , similar for C_1 - C_8 , and much larger for C_1 - C_{10} and C_1 - C_{16} .

RW and LDF have both viscosity and density in their correlations,



Fig. 16. The diffusion coefficients (blue to red solid line) and molar concentration (green to yellow dash line) of C_1 in C_{10} within the first 422 h by different models for C_1 - C_{10} H. The dotted line represents the fitted constant D_L .

and their results are thus influenced by both properties. The D_L variations for RW and LDF are usually not the largest, but typically in the middle (e.g., for C_1 - C_5 and for C_1 - C_8). RW shows the smallest variation for C_1 - C_{10} , but C_1 - C_{16} H no.1 & 2 seem to be exceptional cases for RW, where it gives larger variations than ES.

It is interesting to compare the D_L variations with the constant D_L from the regression. All the constant D_L are within their corresponding D_L ranges from any of the five correlations. Furthermore, the constant D_L values are usually close to the lower limits of the D_L ranges for ES and within the upper half of the ranges for WC and HM. It suggests that, in terms of the overall effect, the lower D_L values estimated by ES dominate the diffusion process while the high D_L values give limited contribution. The constant D_L values are closer to the mean values of the variation ranges for WC/HM than for ES.

For N₂-C_X, the D_L ranges are generally smaller than those for C₁-C_X at the same pressure level, which can be partly attributed to the lower N₂ solubility in n-alkanes. The five correlations show some similar

characteristics as discussed for C1-CX systems, such as

- 1 The range for ES is relatively smaller for the lighter systems (N_2-C_5) and larger for the heavier systems (N_2-C_{10} , N_2-C_{16}) compared to WC/HM.
- 2 For ES, WC, and HM, a higher pressure results in a larger $D_{\rm L}$ variation.
- 3 Constant D_L values are usually close to the lower limits of the ranges for ES, and within the upper half of the ranges for WC and LDF.
- 4 RW and LDF rarely give the largest variations.

Obviously, different correlations lead to different interpretations on the D_L range for the same set of CVD data. However, we cannot claim that a smaller variation is a more correct description. The magnitude of variation is determined by the dependence on density, viscosity, and composition in these correlations. From a practical viewpoint, for those correlations with a narrower range and a better agreement with the

constant D_L, it is easier to select a constant D_L to replace the correlation.

5.6. Diffusion coefficient profiles

The CVD simulation can provide the diffusion coefficient and concentration profiles and their development with time, revealing other differences between different correlations. We select a few cases (generated using regressed D_L), including C_1 - C_5 M no.1, C_1 - C_{10} M, C_1 - C_{10} H, C_1 - C_{16} M no.1, and N_2 - C_5 M no.1 for illustration here. Since WC and HM give almost the same profiles (see Fig. S6 in Supplementary Material). For the ease of illustration, we only plot the results for ES, WC, RW, and LDF in the figures.

5.6.1. C₁-C₅ M no.1 (21.4 °C, 94.9bar)

Fig. 12 shows the C₁ concentration and diffusion coefficient variations within the first 24 h for C₁-C₅ M no.1. The position represents the height in the CVD cell from bottom to top. The interface at around 24 cm moves slightly with time. The liquid-phase and gas-phase regions are located to the left and right sides of the interface, respectively. The D_L value is around 10 cm²/day and the D_G value is more than 70 cm²/day. It should be mentioned that D_G here are not tuned but estimated by ES or LDF.

The C_1 profiles by different correlations are generally similar, with the C_1 concentration in liquid increasing with time and position and that in gas decreasing with time. The closer the position is to the interface, the larger the concentration variation is. For the diffusion coefficient curves, the variation of D_L with time in Fig. 12 seems modest, especially compared with the variation of D_G . ES and LDF give different D_G variations. For ES, D_G increases with time in the whole gas region. For LDF, D_G decreases with time close to the interface but increases in the top region farther from the interface.

Fig. 13 illustrates the variations in liquid more closely. The C₁ concentration in liquid generally increases with time except for the range from around 20 cm and the interface, where the concentration decreases in the period investigated here. At the interface, the liquid-phase equilibrium concentration is higher than the gas-phase equilibrium one. The concentration profiles from different correlations are relatively similar. In contrast, the D_L profiles differ significantly for different correlations. ES gives the most unique D_L trend, with the D_L decreasing towards the interface, just the opposite trend to the other models. The D_L curves by ES at different times cross with each other at around 16 cm, corresponding to an increase with time from around 16 cm to the interface and a decrease in the remaining range. D_I by ES is also higher than the fitted constant D_L for most of the time. RW, LDF, and WC predict an increasing D_L towards the interface. Among them, WC gives the lowest D_L in most positions. Also, the D_L curves by WC at different times obviously cross over each other. This is because DL at the positions close to the interface decreases with time whereas DL at positions close to the bottom increases with time.

Fig. 14 shows the profiles at the late period till the equilibrium state. The D_L profile will approach a horizontal line (constant D_L) at equilibrium. The D_L curves by ES show the smallest variation, whereas those by WC show the biggest variation.

5.6.2. C₁-C₁₀ M (21.4 °C, 97.1bar)

Fig. 15 shows the results for C_1 - C_{10} M for the first 400 h. The pressure level is similar to that for C_1 - C_5 M no.1 but the D_L for C_1 - C_{10} is much smaller. This causes an extremely slow concentration variation close to the bottom. Compared to Fig. 13, the D_L variations by all the models are less than that for C_1 - C_5 M no.1. For WC, the D_L variation is only around 1 cm²/day. RW and LDF give a similar trend to WC, with RW giving the smallest variation. ES again shows a different D_L trend, decreasing towards the interface, from the other models. It also gives the largest D_L variation.

5.6.3. C₁-C₁₀ H (21.5 °C, 180.5bar)

 C_1 - C_{10} H is at a higher pressure (180.5 bar) than C_1 - C_{10} M (97.1 bar). Compared with Fig. 15, Fig. 16 shows that ES gives a higher D_L near the bottom and a little lower D_L close to the interface at the higher pressure. In other words, the DL variation is larger, which agrees with the general observation in Fig. 11. In contrast, WC gives a lower value at the bottom and a higher value at the interface. LDF is similar to WC, but its variation is smaller. The D_L variation by RW is not monotonic and shows a decreasing trend (towards the interface) in a large range from the bottom, somewhat like the trend for ES. However, the trend becomes increasing when it approaches the interface.

5.6.4. C₁-C₁₆ M no.1 (21 °C, 95.6 bar)

The results for C_{1} - C_{16} M no.1 is provided in Fig. S7 in Supplementary Material. All the correlations give lower D_L than the lighter systems. For this heavy system, WC gives a very limited deviation of D_L . RW shows a decreasing trend towards the interface, similar to ES.

5.6.5. N₂-C₅ M no.1 (21 °C, 98.5 bar)

For the N₂-C_x systems, the overall trends by different correlations are similar to those for the corresponding C_1 -C_x systems. The major difference is that the D_L of nitrogen is lower than that for C₁ at the same condition. Fig. S8 in Supplementary Material shows the result of N₂-C₅ M no.1, where ES shows a decreasing D_L towards the interface and the other correlations an increasing trend.

It is worthwhile to discuss the decreasing trend of D_L towards the interface predicted by ES, which is the opposite to most of the predictions by the other models. For instance, WC and HM always predict an increasing trend. According to Eqs. (37) and (39) for ES, the densitydiffusivity product $\rho_M D_{ii}$ depends on the empirical correlations of the reduced density ρ_{pr} and the D_L is then calculated as this product divided by the molar density (a simplified interpretation for binary mixtures). The final $D_{\rm L}$ value depends largely on the molar density $\rho_{\rm M}$ and the reduced density ρ_{pr} . In a mixture of gas (C₁ or N₂) and n-alkane (C₅, C₈, C₁₀, C₁₆), both ρ_M and the critical density ρ_c increase with the dissolution of the gas component. The increase in ρ_{M} is relatively larger, resulting in an increase in $\rho_{\rm pr}$ as well. This leads to a smaller density-diffusivity product, and the final D_L , calculated by dividing a larger ρ_M , becomes even smaller. The above analysis shows that ES predicts a decreasing trend in D_L with the increasing gas mole fraction in the liquid solution. This counterintuitive trend may reflect a problem with the ES correlation.

6. Conclusions

CVD is an important method to determine liquid-phase diffusion coefficients at high pressures. The interpretation of the CVD data requires analytical or numerical solutions, the latter providing a more general solution since it involves fewer assumptions. With this study, we have shown that Michelsen's algorithm for CVD simulation, based on the orthogonal collocation method, can be effectively used to determine the liquid-phase diffusion coefficients D_L using either constant D_L or composition-dependent D_L from different correlations. Based on the simulation analysis of Christoffersen's high-pressure CVD data for C_1 and N_2 in n-alkanes, we have shown that the influence of D_G in the D_L determination is limited and matching the equilibrium pressure is crucial for estimating the correct D_L . For the cases studied here, using the pressure data only seems to be sufficient for determining D_L accurately.

Among the five selected diffusion coefficient correlations, WC and HM are based on the Stokes-Einstein theory, ES and RW are somewhat related to the kinetic theory of dilute gases, and LDF is the only one developed under the MS framework. Nevertheless, in terms of prediction, the more theoretical LDF gives mediocre results. LDF tends to underestimate the pressure (or overestimate D_L) whereas ES tends to

overestimate pressure (or underestimate D_L). The underestimation of D_L by ES becomes smaller for heavier systems. WC and HM give the best performance for most cases. For C_1 - C_X systems, RW is good and comparable with WC and HM. For N_2 - C_X systems, RW is similar to ES.

Regarding the regression results, different correlations give different D_L ranges for the same CVD test, showing that the determined D_L depends on the assumed composition dependence (including the constant D_L assumption). The fitted D_L under the constant D_L assumption is usually close to the lower limit of the D_L range given by ES, and within the upper half of the range by WC or LDF.

The simulated diffusion coefficient profiles have also shown the differences between the tested correlations. In general, ES predicts a decreasing D_L towards the interface whereas WC predicts an increasing trend. RW and LDF usually show an increasing trend. However, for a higher pressure and heavier n-alkanes, RW may give a decreasing trend. These differences illustrate clear but perhaps subtle differences between the correlations, although all of them describe the pressure data equally well and suggest similar concentration profiles.

CRediT authorship contribution statement

Wei Yan: Conceptualization, Methodology, Software, Writing – original draft, Writing – review & editing, Supervision, Project

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.fluid.2023.113944.

Appendix A. Elements in the Jacobian matrix for Eq. (28)-(31)

The non-zero elements in the first N_C rows include

$$J_{ii} = \lambda \frac{\partial \overline{C}_i^z}{\partial C_i^{eL}}, \ i = 1, \dots, N_C$$
(A.1)

$$J_{i,N_C+i} = (1-\lambda) \frac{\partial \overline{C}_i^V}{\partial C_i^{e,V}}, \ i = 1, \dots, N_C$$
(A.2)

$$J_{i,2N_{C}+1} = \overline{C}_{i}^{L} - \overline{C}_{i}^{V} + \lambda \frac{\partial \overline{C}_{i}^{L}}{\partial \lambda} + (1-\lambda) \frac{\partial \overline{C}_{i}^{V}}{\partial \lambda}, \ i = 1, ..., N_{C}$$
(A.3)

For the rows from $N_C + 1$ to $2N_C$, we have

$$J_{N_{C}+i,k} = \frac{\phi_{i}^{e,L} x_{i}^{e}}{\sum_{l=1}^{N_{C}} C_{l}^{e,L}} \left[n_{T} \left(\frac{\partial \ln \phi_{i}^{e,L}}{\partial n_{k}^{e,L}} \right)_{T,P,n_{j \neq k}} - 1 + \frac{\delta_{ik}}{x_{i}^{e}} \right], \ i,k = 1, \dots, N_{C}$$
(A.4)

$$J_{N_{C}+i,N_{C}+k} = -\frac{\phi_{i}^{e,V}y_{i}^{e}}{\sum_{l=1}^{N_{C}}C_{l}^{e,V}} \left[n_{T} \left(\frac{\partial \ln \phi_{i}^{e,V}}{\partial n_{k}^{e,V}} \right)_{T,P,n_{j\neq k}} - 1 + \frac{\delta_{ik}}{y_{i}^{e}} \right], \ i,k = 1,...,N_{C}$$
(A.5)

$$J_{N_{C}+i,2N_{C}+2} = \phi_{i}^{e,L} x_{i}^{e} \left(\frac{\partial \ln \phi_{i}^{e,L}}{\partial P}\right)_{T,\mathbf{n}} - \phi_{i}^{e,V} y_{i}^{e} \left(\frac{\partial \ln \phi_{i}^{e,V}}{\partial P}\right)_{T,\mathbf{n}}, \ i = 1, \dots, N_{C}$$
(A.6)

For the last two rows, we have

$$J_{2N_{C}+1,k} = -\frac{1}{Z_{x}} \left[1 + P\left(\frac{\partial \ln \phi_{k}^{L}}{\partial P}\right)_{T,\mathbf{n}} \right] \left(\frac{\partial \overline{C}_{k}^{L}}{\partial C_{k}^{e,L}} \right), \ k = 1, \dots, N_{C}$$
(A.7)

$$J_{2N_{C}+1,2N_{C}+1} = -\frac{1}{Z_{x}} \sum_{l=1}^{N_{C}} \left[1 + P\left(\frac{\partial \ln \phi_{l}^{L}}{\partial P}\right)_{T,\mathbf{n}} \right] \left(\frac{\partial \overline{C}_{l}^{L}}{\partial \lambda}\right)$$
(A.8)

$$J_{2N_{C}+1,2N_{C}+2} = -\frac{\left(\sum_{i=1}^{N_{C}} \overline{C}_{i}^{L}\right)^{2}}{nR\left(\frac{\partial P}{\partial V^{L}}\right)_{T}}$$
(A.9)

administration. Yibo Yang: Conceptualization, Methodology, Validation, Writing – original draft, Writing – review & editing. Erling H. Stenby: Project administration, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

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$$J_{2N_{C}+2,k} = -\frac{1}{Z_{y}} \left[1 + P\left(\frac{\partial \ln \phi_{k}^{V}}{\partial P}\right)_{T,\mathbf{n}} \right] \left(\frac{\partial \overline{C}_{k}^{V}}{\partial C_{k}^{e,L}}\right), \ k = 1, ..., N_{C}$$

$$J_{2N_{C}+2,2N_{C}+1} = -\frac{1}{Z_{y}} \sum_{l=1}^{C} \left[1 + P\left(\frac{\partial \ln \phi_{l}^{V}}{\partial P}\right)_{T,\mathbf{n}} \right] \left(\frac{\partial \overline{C}_{l}^{V}}{\partial \lambda}\right)$$
(A.10)
$$(A.11)$$

$$J_{2N_{c}+2,2N_{c}+2} = -\frac{\left(\sum_{l=1}^{N_{c}} \overline{C}_{l}^{V}\right)^{2}}{nR\left(\frac{\partial P}{\partial V^{V}}\right)_{T}}$$
(A.12)

It should be noted that Eqs. (A.4) to (A.6) are from the fugacity equalities at the interface, and all the involved composition and pressure derivatives in them are calculated using x_i^e and y_i^e (or $C_i^{e,L}$ and $C_i^{e,V}$). In contrast, the thermodynamic properties and derivatives in Eqs. (A.7) and (A.12) correspond to the average concentrations \bar{C}_i^L and \bar{C}_i^V .

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