

SUPPORTING INFORMATION

Full Characterization of CO₂–Oil Properties On-Chip: Solubility, Diffusivity, Extraction Pressure, Miscibility, and Contact Angle

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S1. Oil-wet of glass and silicon surfaces

Figure S1 shows the oil-wet condition of glass and silicon surfaces at atmospheric condition, indicating that both surfaces exhibit similar wettability. While the top glass surface could have some influence on the observed contact angle, the effect is expected to be negligible, particularly as both silicon and glass surfaces exhibited a similar oil-wet condition.

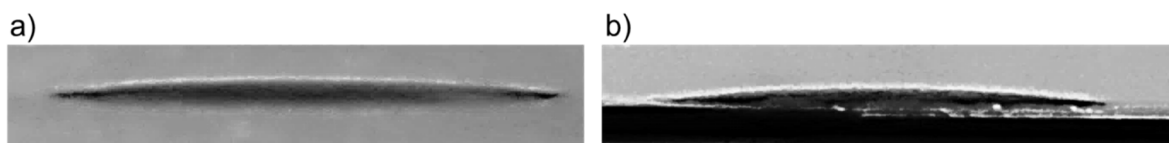


Figure S1. Oil-wet condition of a) glass and b) silicon surfaces at atmospheric condition.

S2. Determination of minimum miscibility pressure from oil swelling/extraction curve

CO₂–oil MMP can be estimated from the oil swelling/extraction data and the point where major component extraction gives way to minor. Here, the transition point was estimated by fitting a straight line in the minor extraction zone, and determining the intercept with the extraction line as shown in Figure S2. The quality of the linear fit (R^2) was used to determine which pressures to include in the minor zone linearization. Using this analysis, 7.4 MPa and 10.6 MPa are the MMP values of this crude oil and CO₂ system at temperatures of 23 and 50 °C, respectively.

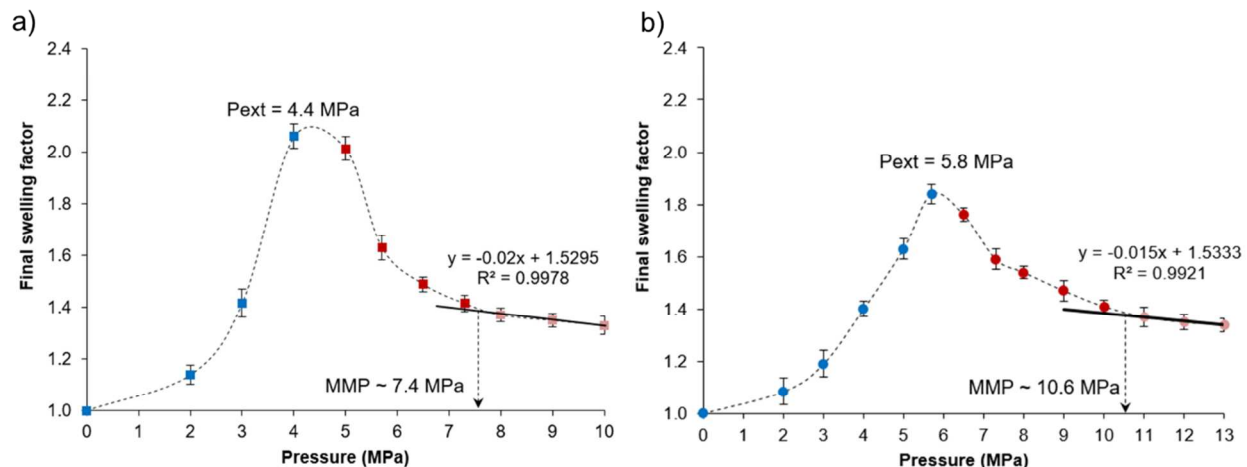


Figure S2. CO₂–oil MMP determination from oil swelling/extraction data at a) 23 °C and b) 50 °C.

S3. Mathematical modeling of 1-D oil swelling

The mathematical approach used in this work is based on a model presented by Jamialahmadi et al.¹ to determine CO₂ solubility and diffusion coefficients from swelling data. The variation of oil plug length inside the micro-PVT channel is equal to the rate of variation of the liquid phase volume, which is given:

$$\frac{dx}{x} = \frac{dV}{V} = d(v_s C_{s,av}) \quad (1)$$

in which $C_{s,av}$ is the average concentration of the CO₂ in the oil sample (kg/m³) and v_s is the specific volume of CO₂ at the experimental pressure and temperature (m³/kg). Integrating Eq. (1) gives:

$$C_{s,av} = \frac{\int_0^V C_s dV}{V} = \frac{1}{v_s} \ln \frac{x}{x_0} = \frac{1}{v_s} \ln(SF) \quad (2)$$

Where x_0 and x_t are the initial oil length and oil length at time equal to t , respectively. SF is the swelling factor. Eq. (2) is used to calculate the average concentration of CO₂ in the oil phase.

The 1-D diffusion process was described using the following form of Fick's law. Here, we considered that the diffusion coefficient (D) to be constant during the entire process with no chemical reaction:

$$\frac{\partial C_s}{\partial t} = D \frac{\partial^2 C_s}{\partial x^2} \quad (3)$$

The initial and boundary condition for infinite system is:

For $0 < x < x_t$ and $t < 0$, $C_{s,av} = 0$

For $x = x_t$ and $t \geq 0$, $C_s = C_{si}$, (C_{si} is the interfacial concentration)

For $x = 0$ and $t \geq 0$ $C_s = 0$

Considering the above initial and boundary conditions, the solution is given by Crank²:

$$C_s(x, t) = C_{si} \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (4)$$

Total mass of CO₂ diffused in oil phase calculated by integrating Eq. (4) over the volume of the oil plug:

$$m_A = \int_0^V C_s(x, t) dV = S \int_0^x C_s(x, t) dx = 2SC_{si} \sqrt{\frac{Dt}{\pi}} \quad (5)$$

S is the cross section of the oil plug. Combining Eq. (1) with Eq. (5) gives a relation between the CO₂ average concentration and time, diffusion coefficient and interfacial concentration (C_{si}):

$$C_{s,av} = \frac{2 C_{si}}{x_o \exp(v_s C_{s,av})} \sqrt{\frac{Dt}{\pi}} = \left(\frac{2 C_{si}}{x_o \exp(v_s C_{s,av})} \sqrt{\frac{t}{\pi}} \right) \sqrt{D} = m\sqrt{D} \quad (6)$$

The interfacial CO₂ concentration at the interface is the CO₂ solubility under the test condition which can be calculated by substituting the final swelling factor in Eq. (2). Plotting the average concentration versus the m (term in the parenthesis) gives a slope which is equal to the square root of the diffusion coefficient.

For the finite case analysis, the boundary condition is:

$$\text{For } x = 0 \text{ and } t \geq 0 \rightarrow \frac{\partial C_{s,av}}{\partial x} = 0,$$

Integration of Eq. (3) with respect to x gives:

$$\int_0^x \frac{\partial C_{s,av}}{\partial t} dx = D \int_0^x \frac{\partial^2 C_{s,av}}{\partial x^2} dx = D \frac{\partial C_{s,av}}{\partial x} \Big|_x \quad (7)$$

Using Leibnitz's integration rule to expand the LHS of Eq. (7):

$$\frac{d}{dt} \int_0^x C_{s,av} dx = D \frac{\partial C_{s,av}}{\partial x} \Big|_{x_t} + C_{si} \frac{dx_t}{dt} \quad (8)$$

Differentiation of Eq. (3) with respect to time gives:

$$\frac{dC_{s,av}}{dt} = \frac{1}{x_t} \frac{d}{dt} \int_0^x C_{s,av} dx - \frac{C_{s,av}}{x_t} \frac{dx_t}{dt} \quad (9)$$

Substituting the second term in the right-hand side by Eq. (8) leads to:

$$x_t \frac{dC_{s,av}}{dt} = (C_{si} - C_{s,av}) \frac{dx_t}{dt} + D \frac{\partial C_{s,av}}{\partial x} \Big|_{x_t} \quad (10)$$

Substituting for the derivative of x_t from Eq. (2)

$$x_t \frac{dC_{s,av}}{dt} = (C_{si} - C_{s,av}) x_t v_s \frac{dC_{s,av}}{dt} + D \frac{\partial C_{s,av}}{\partial x} \Big|_{x_t} \quad (11)$$

Now if we divide both sides by x_t and substitute for x_t from Eq. (2):

$$\frac{dC_{s,av}}{dt} = (C_{si} - C_{s,av})v_A \frac{dC_{s,av}}{dt} + \frac{D}{x_0 \exp(v_a C_{s,av})} \frac{\partial C_{s,av}}{\partial x} \Big|_{x_t} \quad (12)$$

To calculate the last term in the right-hand side of the Eq. (12), the development presented by Jamialahmadi et al.¹ was followed. It was assumed that for a moving boundary system, the concentration profile of the diffusing substance can be described as:

$$C_s = b_0 + b_1 x^n \quad (13)$$

in which b_0 and b_1 are constants and n is defined as:

$$n = a\omega, \quad \omega = \frac{C_{si}}{C_{s,av}} \quad (14)$$

The parameter a is positive and independent of time and should be evaluated from the experimental data. After some mathematical manipulations, the following expression can be achieved for the last term in the RHS of the Eq. (12):

$$\frac{\partial C_{s,av}}{\partial x} \Big|_{x_t} = \frac{(C_{si} - C_{s,av})(aC_{si} - C_{s,av})(1 - v_s C_{s,av})}{x_0 C_{s,av}} \quad (15)$$

we could rewrite the Eq. (12), by replacing the Eq. (15) in the last term of Eq. (12) and rearranging it:

$$\frac{dC_{s,av}}{dt} = \frac{D(C_{si} - C_{s,av})(aC_{si} + C_{s,av})(1 - v_s C_{s,av})^2}{x_0 C_{s,av} (1 - v_s (C_{si} - C_{s,av}))} \quad (16)$$

After rearranging Eq. (16):

$$\frac{x_0 C_{s,av} (1 - v_s (C_{si} - C_{s,av}))}{(C_{si} - C_{s,av})(aC_{si} + C_{s,av})(1 - v_s C_{s,av})^2} dC_{s,av} = D dt \quad (17)$$

Integrating both sides of Eq. (17):

$$\int_0^{C_{si}} \frac{x_0 C_{s,av} (1 - v_s (C_{si} - C_{s,av}))}{(C_{si} - C_{s,av})(aC_{si} + C_{s,av})(1 - v_s C_{s,av})^2} dC_{s,av} = D t \quad (18)$$

The slope of the generated line obtained by plotting the numerical integration of the LHS of Eq. (18) versus time, gives the diffusion coefficient. The results are plotted in Figure S3 below.

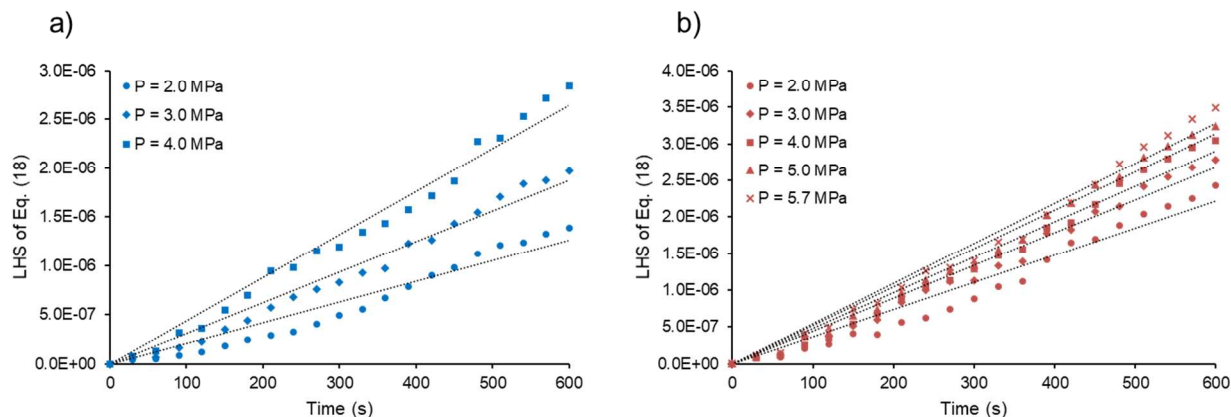


Figure S3. Linear least-square fit of LHS of Eq. (18) vs. time for tests at a) 23 °C, and b) 50 °C.

Table S1 presents all the input parameters as well as calculated solubility and diffusivity values of CO₂–oil system under all experimental conditions.

Table S1. Input parameters and calculated solubility and diffusivity values of CO₂–oil system under all experimental conditions

T (°C)	P (MPa)	v_s (m ³ /kg)*	C_{si} (kg/m ³)	a	$D \times 10^9$ (m ² /s)
23	2.0	0.0249	12.4	0.25	2.1
	3.0	0.0154	33.2	0.30	3.1
	4.0	0.0105	69.2	0.30	4.4
50	2.0	0.0281	3.0	0.40	3.7
	3.0	0.0178	9.9	0.40	4.4
	4.0	0.0127	26.5	0.50	4.8
	5.0	0.0095	51.2	0.45	5.2
	5.7	0.0080	76.4	0.55	5.5

* Specific volume of CO₂ is taken from National Institute of Standards and Technology (NIST).

S4. Compositional analysis of representative West Texas crude oil (stock tank condition)

The compositional analysis of representative West Texas crude oil is taken from literature (Lansangan and Smith³) and presented in Table S2.

Table S2. Compositional analysis of representative West Texas crude oil under atmospheric condition (stock tank condition).

Component	Composition (mole%)
C ₁	0
C ₂	0
C ₃	0
C ₄	0
C ₅	0.0587
C ₆	0.0909
C ₇	0.0933
C ₈	0.1030
C ₉	0.0849
C ₁₀	0.0704
C ₁₁	0.0560
C ₁₂	0.0445
C ₁₃	0.0328
C ₁₄	0.0405
C ₁₅₊	0.325
Average molecular weight	199.3 g/mol

References:

- (1) Jamialahmadi, M. Emadi, M.; Müller-steynhagen, H. Journal of Petroleum Science and Engineering 2006, 53, 47–60.
- (2) Crank, J. The Mathematics of Diffusion; Oxford University Press, USA, 1975.
- (3) Lansangan, R. M.; Smith, J. L. SPE Reserv. Eng. 1993, 8, 175–182.