

Supplementary Information

Exploring Effects of Four Important Factors on Oil–CO₂ Interfacial Property and
Miscibility in Nanopores

by

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Derivation of interfacial thickness

In this study, a formula for determining the interfacial thickness between two mutually soluble phases (e.g., oil and CO₂ phases) is derived by taking account of the two-way mass transfer. Suppose that a closed system, as shown in Fig. S1, consists of two mutually soluble phases (α and β), each of which has two components (1 and 2), the Gibbs free energy as an interfacial excess quantity is given by,¹

$$G(p, T) = \gamma A + \mu_1 N_1 + \mu_2 N_2 = U + PV - TS \quad (\text{S1})$$

where γ is the interfacial tension, A is the surface area of the interface, μ is the chemical potential, N_j is the mole number of the j^{th} component, U is the internal energy, P is the pressure, V is the volume, T is the temperature, S is the entropy. Two-way mass transfer occurs so that there is not only internal energy (U) change but also external potential energy (Y) change,

$$(U^\alpha + Y^\alpha) + (U^\beta + Y^\beta) = TS - PV + \gamma A + (\mu_1^\alpha N_1^\alpha + \mu_1^\beta N_1^\beta) + (\mu_2^\beta N_2^\beta + \mu_2^\alpha N_2^\alpha) \quad (\text{S2})$$

Legendre transforms of the internal energy plus external potential energy gives,

$$d[(U^\alpha + Y^\alpha) + (U^\beta + Y^\beta)] = TdS - PdV + \gamma dA + (\mu_1^\alpha dN_1^\alpha + \mu_1^\beta dN_1^\beta) + (\mu_2^\beta dN_2^\beta + \mu_2^\alpha dN_2^\alpha) \quad (\text{S3})$$

Given the fact that $(N_1^\alpha + N_1^\beta)$ and $(N_2^\alpha + N_2^\beta)$ are constant because of mass conservation, Eq.

(S3) is rewritten as,

$$d[(U^\alpha + Y^\alpha) + (U^\beta + Y^\beta)] = TdS - PdV + \gamma dA + (\mu_1^\alpha - \mu_1^\beta) dN_1^\alpha + (\mu_2^\beta - \mu_2^\alpha) dN_2^\beta \quad (\text{S4})$$

In Eq. (S4), $[(\mu_1^\alpha - \mu_1^\beta) dN_1^\alpha + (\mu_2^\beta - \mu_2^\alpha) dN_2^\beta]$ is referred to as the chemical potential changes due to the interfacial mass transfer. Physically, $[(\mu_1^\alpha - \mu_1^\beta) dN_1^\alpha]$ or $[(\mu_2^\beta - \mu_2^\alpha) dN_2^\beta]$ represents the change of the internal energy and external potential energy for each component.

Then, subtracting differentiation of $(\gamma A + \mu_1 N_1 + \mu_2 N_2)$ from the full differentiation of $[(U + Y) + PV - TS]$ yields,

$$-SdT + VdP - N_1 d\mu_1 - N_2 d\mu_2 = Ad\gamma \quad (\text{S5})$$

The Gibbs-Duhem equation for each phase can be written,²

$$-S^\alpha dT + V^\alpha dP^\alpha + N_1^\alpha d\mu_1 + N_2^\alpha d\mu_2 = 0 \quad \text{Phase } \alpha \quad (\text{S6a})$$

$$-S^\beta dT + V^\beta dP^\beta + N_2^\beta d\mu_2 + N_1^\beta d\mu_1 = 0 \quad \text{Phase } \beta \quad (\text{S6b})$$

Two undetermined Lagrange multipliers, λ^α and λ^β , are introduced and applied into Eqs. (S6a) and (S6b). Afterwards, Eq. (S5) is used to subtract them, which is then divided by interfacial area A ,

$$d\gamma = \frac{-(S - \lambda^\alpha S^\alpha - \lambda^\beta S^\beta)}{A} dT + \frac{(V - \lambda^\alpha V^\alpha - \lambda^\beta V^\beta)}{A} dP - \frac{(N_1 - \lambda^\alpha N_1^\alpha - \lambda^\beta N_1^\beta)}{A} d\mu_1 - \frac{(N_2 - \lambda^\alpha N_2^\alpha - \lambda^\beta N_2^\beta)}{A} d\mu_2 \quad (\text{S7})$$

Let,

$$\bar{s} = (S - \lambda^\alpha S^\alpha - \lambda^\beta S^\beta) / A \quad (\text{S8a})$$

$$\delta = (V - \lambda^\alpha V^\alpha - \lambda^\beta V^\beta) / A \quad (\text{S8b})$$

$$\Gamma_1 = (N_1 - \lambda^\alpha N_1^\alpha - \lambda^\beta N_1^\beta) / A \quad (\text{S8c})$$

$$\Gamma_2 = (N_2 - \lambda^\alpha N_2^\alpha - \lambda^\beta N_2^\beta) / A \quad (\text{S8d})$$

Then, Eq. (S7) can be represented as,

$$d\gamma = -\bar{s}dT + \delta dP - \Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \quad (\text{S9})$$

Theoretically, two Lagrange multipliers λ^α and λ^β could be determined by setting any two of the interfacial excess quantities (i.e., $\bar{s}, \delta, \Gamma_1, \Gamma_2$) to be zero, the choices of which are purely

conventional.³ At a given P and T , the chemical potentials cannot be determined and should be eliminated as independent variables so that Γ_1 and Γ_2 are set to be zero,

$$d\gamma = -\bar{s}dT + \delta dP \quad (\text{S10})$$

T remains constant in the study, i.e., $dT = 0$, so,

$$\delta = \left(\frac{\partial\gamma}{\partial P}\right)_T \quad (\text{S11})$$

In Eq. (S11), δ is the distance between two miscible phases, which is also denoted as the interfacial thickness.

In addition to the above derivations, there is another series of derivations for the interfacial thickness based on the Gibbs convention is proposed. First, dividing Eqs. (S6a) and (S6b) by volume V^α and V^β at the constant temperature,

$$-dP^\alpha = n_1^\alpha d\mu_1 + n_2^\alpha d\mu_2 \quad \text{Phase } \alpha \quad (\text{S12a})$$

$$-dP^\beta = n_2^\beta d\mu_2 + n_1^\beta d\mu_1 \quad \text{Phase } \beta \quad (\text{S12b})$$

where n_1^α and n_1^β are the molar concentrations of the first component in α and β phases, respectively; n_2^α and n_2^β are the molar concentrations of the second component in α and β phases, respectively.

Gibbs convention at a constant temperature states,⁴

$$-\left(\frac{\partial\gamma}{\partial P}\right)_T = \sum_{i=1}^i \Gamma_i \left(\frac{\partial\mu_i}{\partial P}\right)_T \quad (\text{S13})$$

Assuming the location of $\Gamma_1 = 0$ to be the reference surface,

$$N_1 = z_1 n_1^\beta + (H - z_1) n_1^\alpha \quad (\text{S14})$$

where z_1 is the surface location and H is the total height. For Component 1, with respect to the surface at z_2 and a random location b ,

$$\begin{aligned} N_1 &= z_2 n_1^\beta + (H - z_2) n_1^\alpha + \Gamma_1^{(z_2)} \\ &= b n_1^\beta + (H - b) n_1^\alpha + \Gamma_1^{(b)} \end{aligned} \quad (\text{S15})$$

Similar equations can be obtained for substance 2.

Eqs. (S14) and (S15) are subtracted to obtain $\Gamma_1^{(b)} = \delta(n_1^\alpha - n_1^\beta)$. Similarly, $\Gamma_2^{(b)} = \delta(n_2^\alpha - n_2^\beta)$.

Given that $P^\alpha = P^\beta = P$, Eqs. (S12a) and (S12b) are rearranged to be,

$$\left(\frac{\partial \mu_1}{\partial P}\right) = \frac{n_2^\alpha - n_2^\beta}{n_1^\alpha n_2^\beta - n_2^\alpha n_1^\beta} \quad (\text{S16a})$$

$$\left(\frac{\partial \mu_2}{\partial P}\right) = \frac{n_1^\beta - n_1^\alpha}{n_1^\alpha n_2^\beta - n_2^\alpha n_1^\beta} \quad (\text{S16b})$$

Then, Eqs. (S16a) and (S16b) are combined into Eq. (S13),

$$\left(\frac{\partial \gamma}{\partial P}\right) = -\Gamma_1^{(z_2)} \left(\frac{n_2^\alpha - n_2^\beta}{n_1^\alpha n_2^\beta - n_2^\alpha n_1^\beta}\right) \quad (\text{S17a})$$

$$\left(\frac{\partial \gamma}{\partial P}\right) = -\Gamma_2^{(z_1)} \left(\frac{n_1^\beta - n_1^\alpha}{n_1^\alpha n_2^\beta - n_2^\alpha n_1^\beta}\right) \quad (\text{S17b})$$

Since $\delta = \frac{\Gamma_i^b - \Gamma_i^d}{\Delta n_i}$, b or d means any location in the system. Thus the interfacial thickness is,

$$\delta = -\left(\frac{\partial \gamma}{\partial P}\right)_T \left[\frac{n_1^\alpha n_2^\beta - n_2^\alpha n_1^\beta}{(n_1^\beta - n_1^\alpha)(n_2^\alpha - n_2^\beta)} \right] \quad (\text{S18})$$

In this study, phase α is the vapour phase, phase β is the liquid phase, substance 1 is CO₂,

and substance 2 is oil. For a light oil–CO₂ system, $\left[\frac{n_{\text{CO}_2}^{\text{V}} n_{\text{oil}}^{\text{L}} - n_{\text{CO}_2}^{\text{L}} n_{\text{oil}}^{\text{V}}}{(n_{\text{CO}_2}^{\text{L}} - n_{\text{CO}_2}^{\text{V}})(n_{\text{oil}}^{\text{V}} - n_{\text{oil}}^{\text{L}})} \right] \approx -1$. Thus Eq. (S18)

is simplified to be $\delta = \left(\frac{\partial\gamma}{\partial P}\right)_T$, which represents the interfacial thickness between two mutually soluble phases as defined in Eq. (S11).

It should be noted that the sign of δ is determined by the characteristics of the two bulk phases. More specifically, if the two phases are barely mutually soluble and repulsive intermolecular interaction dominates in the interfacial region, $\delta > 0$. If the two phases are mutually soluble and two-way mass transfer occurs across the interface, $\delta < 0$. In this study, the interfacial tension of the light oil–CO₂ system is decreased with the pressure so that δ is negative. Although the sign of δ can be positive, zero, or negative, the physical interfacial thickness has to be positive.³

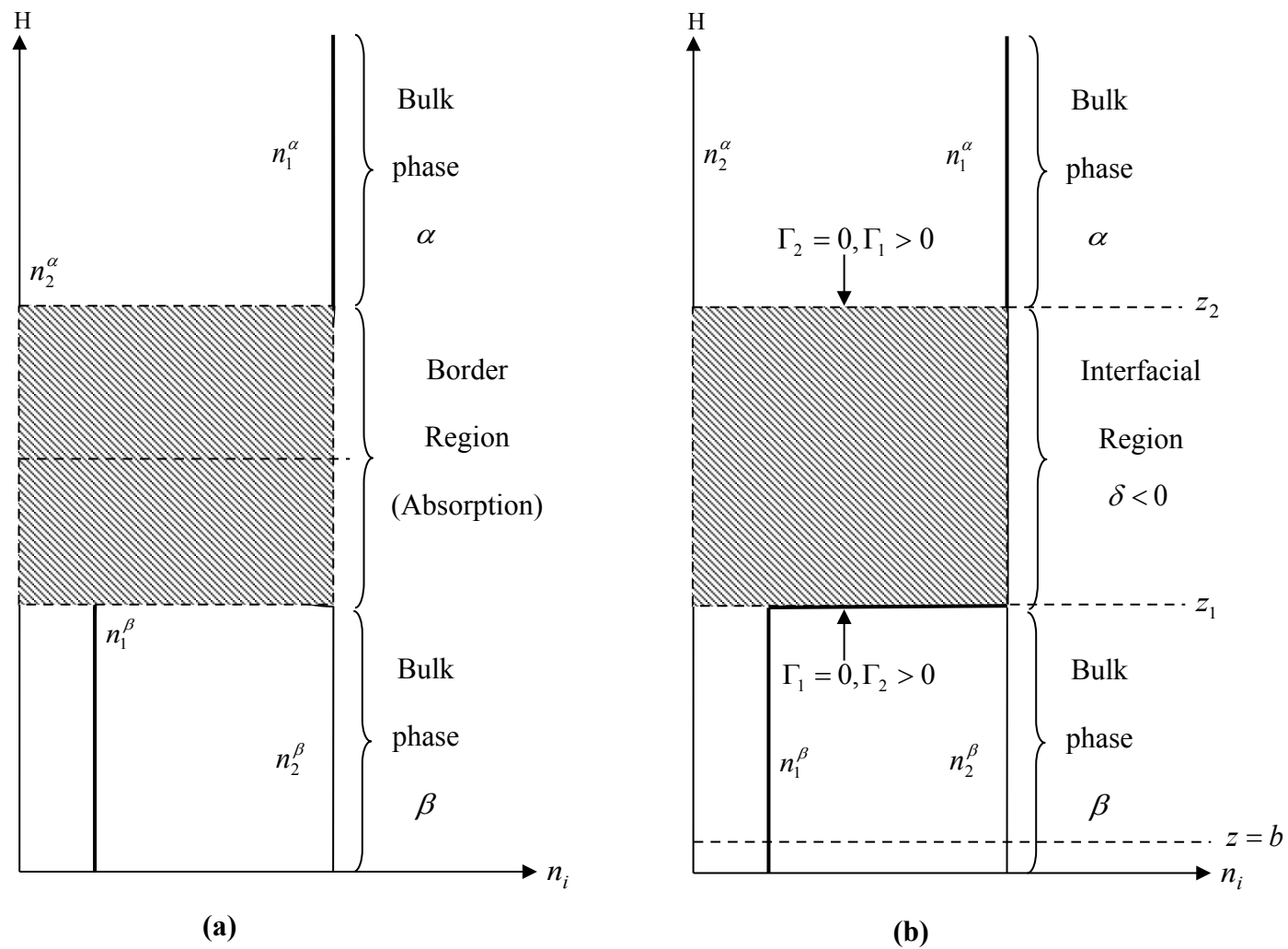


Fig. S1 Schematic diagram of the interfacial structure between two miscible phases: **(a)** real case and; **(b)** ideal case.

References

- (1) E. A. Guggenheim, *Thermodynamics—an Advanced Treatment for Chemists and Physicists*, North-Holland, Amsterdam, 1985.
- (2) J. Lyklema, *Fundamental of Interface and Colloid Science. Volume I: Fundamentals*, San Diego: Academic Press Inc., 1991.
- (3) C. Yang, D. Li, *Colloid Surf. A: Physicochem. Eng. Aspects* 1996, **113**, 51–59.
- (4) J. W. Gibbs, *The scientific papers of J Willard Gibbs: Vol. 1: Thermodynamics*, Dover Publications, New York, 1961.