

# Supplementary Information for "Competitive Sorption of CO<sub>2</sub> with Gas Mixtures in Nanoporous Shale for Enhanced Gas Recovery from Density Functional Theory"

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# Solubility of $\text{CH}_4$ and $\text{CO}_2$ in water

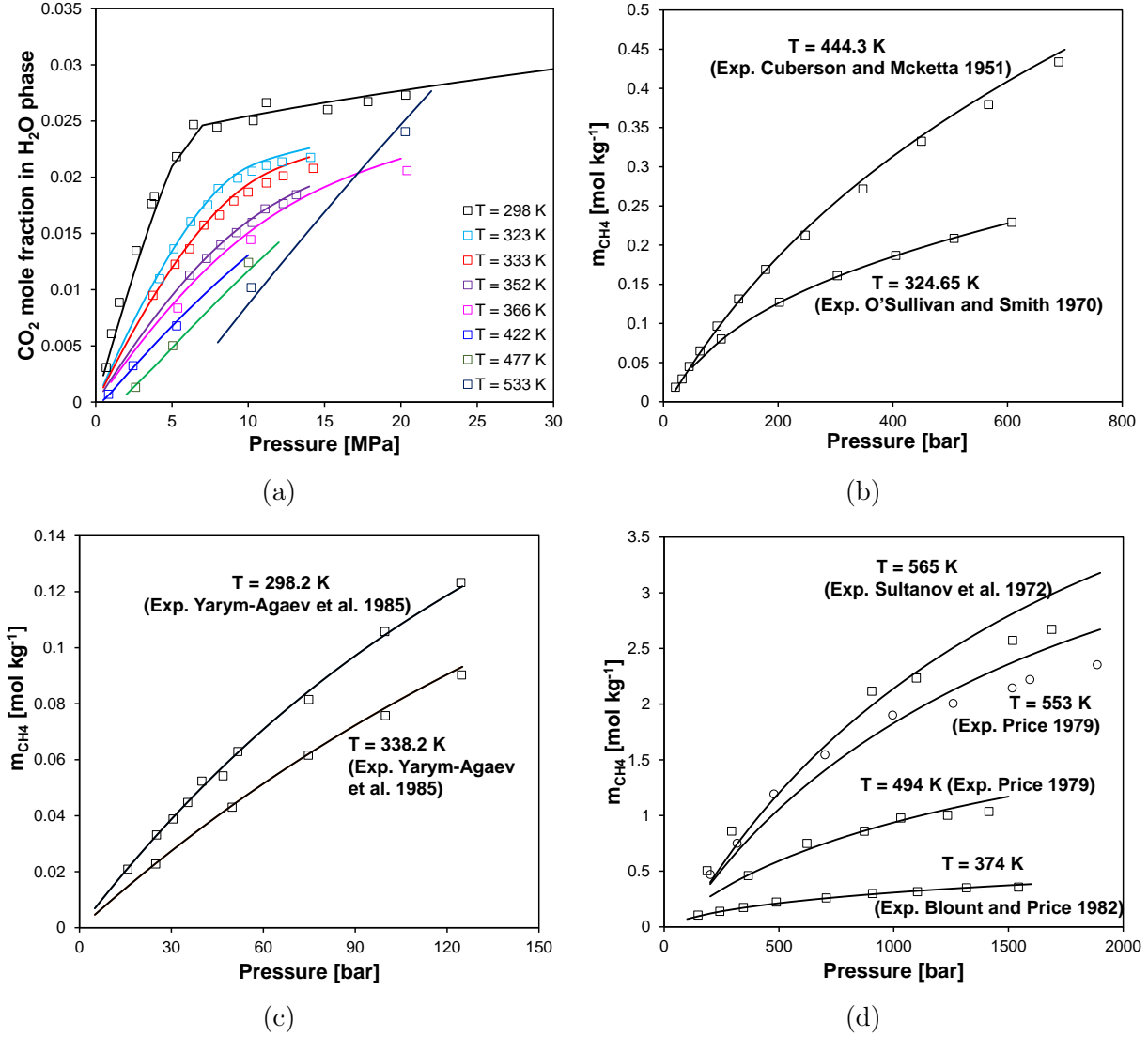


Figure 1: Solubility of  $\text{CO}_2$  and  $\text{CH}_4$  in water at different temperatures from experiments (points) and PC-SAFT (curves).

## PC-SAFT model and parameters for kerogens

For nonassociating molecules, three parameters are needed to describe a molecule, which are segment number ( $m$ ), segment diameter ( $\sigma$ ), and attraction energy between segments ( $\epsilon/k_b$ ). For kerogens these three parameters are correlated with molecular weight ( $Mw$ ) and

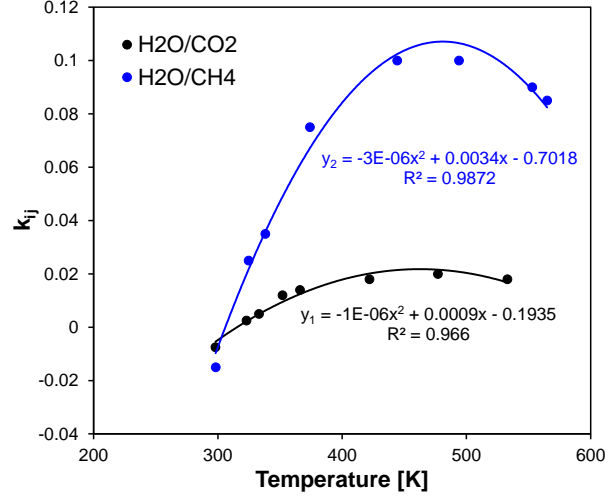


Figure 2: Fitted binary interaction parameters for PC-SAFT of water-CO<sub>2</sub> and water-CH<sub>4</sub> as a function of temperature.

Table 1: PC-SAFT parameters for kerogens in Part II.C

kerogen	source	type	Mw [g/mol]	density [g/cm <sup>3</sup> ]	$\gamma$ [-]	$m_{\text{cross-linker}}$ [g/100g]	$\Phi$ [-]
IIA	Paris Basin Toarcian	Type II immature	3500	1.10	0.69	2.3	12.48
IIB		Type II partially mature	3500	1.15	0.76	2.775	11.26
IIC		Type II most mature	3500	1.20	0.82	2.95	11.23
GRK	Green River	Type I immature	3800	1.00	0.41	0.575	24.17

aromaticity ( $\gamma$ ) in the same way as for asphaltene models:<sup>1</sup>

$$m = (1 - \gamma)(0.057M_w + 0.8444) + \gamma(0.0101M_w + 1.7296) \quad (1)$$

$$\sigma = (1 - \gamma) \left( 4.047 - 4.8013 \frac{\ln(M_w)}{M_w} \right) + \gamma \left( 4.6169 - \frac{93.98}{M_w} \right) \quad (2)$$

$$\varepsilon/k_b = (1 - \gamma) \exp \left( 5.5769 - \frac{9.523}{M_w} \right) + \gamma \left( 508 - \frac{234100}{M_w^{1.5}} \right) \quad (3)$$

For crosslinked polymers, elastic free energy is added to account for the volume change of a cross-linked kerogen network when mixing with solvents. The total free energy in a kerogen network with solvents is a sum of different contributions,

$$A^{total} = A^{id} + A^{seg} + A^{ch} + A^{disp} + A^{elast} \quad (4)$$

where  $A^{id}$  is the ideal gas contribution,  $A^{seg}$  is the residual free energy of spherical segments,  $A^{ch}$  is the change in free energy on bonding segments to form molecules,  $A^{disp}$  is from the long-range attraction between molecules, and  $A^{elast}$  is the free energy change due to cross-linked polymer network swelling when solvent molecules enter the polymer matrix. Details of the segment, chain and dispersion terms are given in early SAFT papers.<sup>2,3</sup> The elastic free energy is taken from Miao et al.,<sup>4</sup> where a finite extensibility of the network is considered.

$$\frac{A^{elastic}}{k_b T} = n_{chain} \frac{\Phi - 2}{\Phi} \left[ \frac{3}{2} \times \frac{(V/V_0)^{2/3} - 1}{1 - (V/V_{max})^{2/3}} - \ln \left( \frac{V}{V_0} \right) \right] \quad (5)$$

where  $n_{chain}$  is the number of polymer chains between two crosslinkers,  $k_b$  is the Boltzmann constant,  $\Phi$  is the network functionality which is treated as a fitting parameter, representing the deviation from a perfect polymer network (a perfect network would have a functionality value of 4; a larger functionality indicates more entanglements of the chains).  $V$  is the molar volume of each polymer chain after swelling,  $V_0$  is the molar volume of dry polymer chain,  $V_{max}$  is the maximum volume that the swollen polymer network can reach and is calculated

by assuming an ideal tetrahedral network,

$$V_{\max} = n_{\text{cross-linker}} N_A \left( \frac{\sqrt{2}^3}{2} \sin \left( \frac{109.5^\circ}{2} \frac{\pi}{180^\circ} \right) m_p \sigma_p \right)^3 \quad (6)$$

The chain length between cross-links is given by the product of the number of monomer segments in each chain  $m_p$  and their segment diameter  $\sigma_p$ .  $n_{\text{cross-linker}}$  is the number of cross-linker molecules, which can be calculated by the total mass of linkers and the linker molecular weight.

$$n_{\text{cross-linker}} = \frac{m_{\text{cross-linker}}}{M_{\text{cross-linker}}} \quad (7)$$

The number of chains between linkers is determined by the total number of linkers and its functionality,

$$n_{\text{chain}} = n_{\text{cross-linker}} \cdot \frac{\Phi}{2} \quad (8)$$

Then the molecular weight of polymer chains between linkers can finally be calculated by

$$M_c = \frac{m_{\text{polymer}} + m_{\text{cross-linker}}}{n_{\text{chain}}} \quad (9)$$

where  $m_{\text{polymer}}$  is the total mass of polymer before adding linker molecules.

The elastic contribution to the total pressure of the cross-linked polymer network phase is thus obtained by

$$p^{\text{elast}} = - \left( \frac{\partial A^{\text{elast}}}{\partial V} \right)_{T, n_i} \quad (10)$$

As kerogen is insoluble in any solvent, the phase equilibrium between the solvent phase (I) and the swollen kerogen phase(II) is obtained by equalizing the total pressure and the chemical potential of each solvent in both phases.

$$p^{\text{I}} = p^{\text{II}} \quad (11)$$

$$\mu_{(\text{solvent})_i}^{\text{I}} = \mu_{(\text{solvent})_i}^{\text{II}} \quad i = 1, 2, \dots, N \quad (12)$$

where  $N$  is the total number of solvent species.

## Bulk properties of CO<sub>2</sub> by PC-SAFT EoS

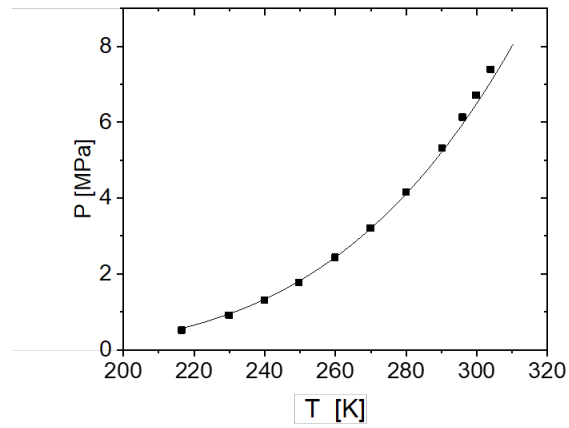


Figure 3: Vapor pressure of CO<sub>2</sub> from PC-SAFT EoS and NIST.

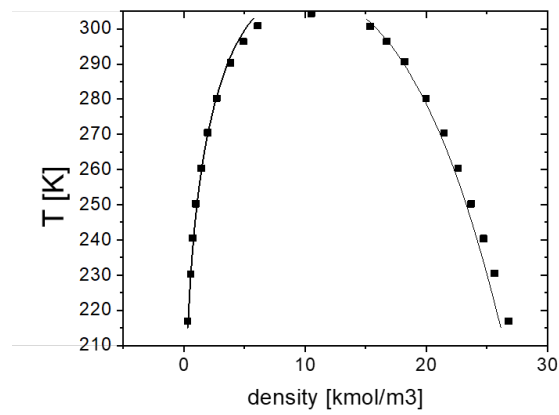


Figure 4: Equilibrium vapor and liquid densities of CO<sub>2</sub> from PC-SAFT EoS and NIST.

## References

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