Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information:

Diffusivity and Hydrophobic Hydration of Hydrocarbons in Supercritical CO2 and Aqueous Brine

Hyeonseok Lee[2], Mehdi Ostadhassan[1,3*], Zheng Sun[4], Hui Pu[2], Bo Liu[1], Rajender S. Varma[5], Ho Won Jang[6*], Mohammadreza Shokouhimher[2,6*]

[1]*Department of Petroleum Engineering, University of North Dakota, Grand Forks, ND 58202, United States*

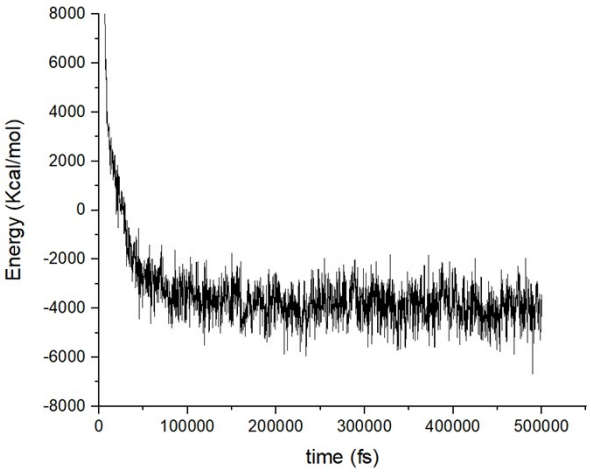
[2]*Key Laboratory of Continental Shale Hydrocarbon Accumulation and Efficient Development, Northeast Petroleum University, Daqing 163318, China*

[*]Corresponding authors' e-mail addresses: mehdi.ostadhassan@nepu.edu.cn

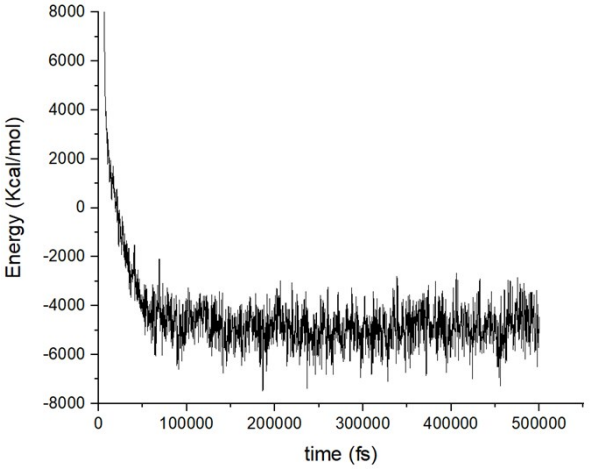
Potential Energy Profile

Before evaluating the results of the simulations, it is necessary to demonstrate that the system reaches the equilibrium, with a proper distribution of kinetic and potential energy. In Fig. S1 we present plots of the total energy of the systems for different brine concentration for Benzene and Pentane. We found that the all systems reach equilibrium around first 50 ps for the NVP simulations.

(a) Benzene in SC-CO2 with 2% Brine

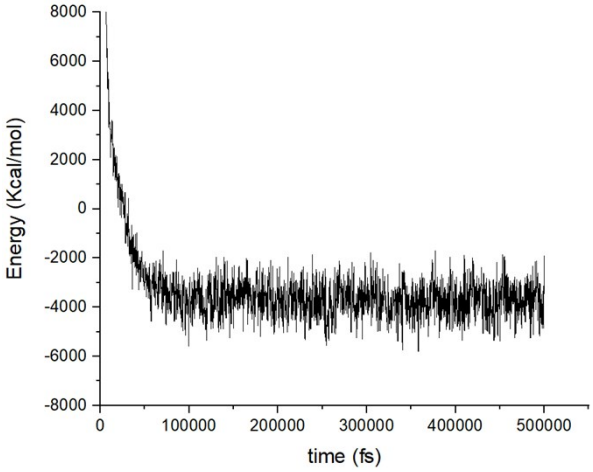


(b) Benzene in SC-CO2 with 5% Brine

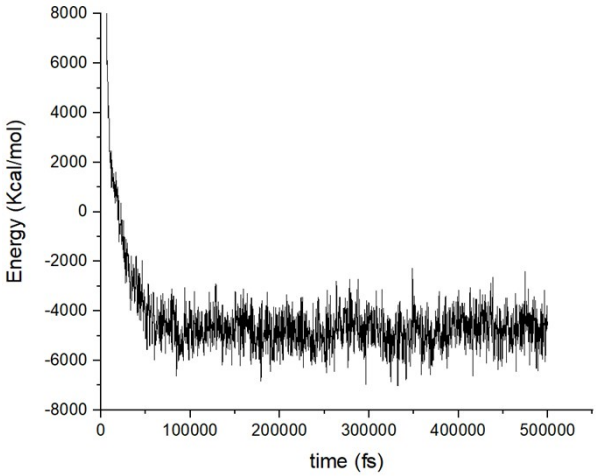


(c) Benzene in SC-CO2 with pure water

(d) Pentane in SC-CO2 with 2% Brine



(e) Pentane in SC-CO2 with 5% Brine



(f) Pentane in SC-CO2 with pure water

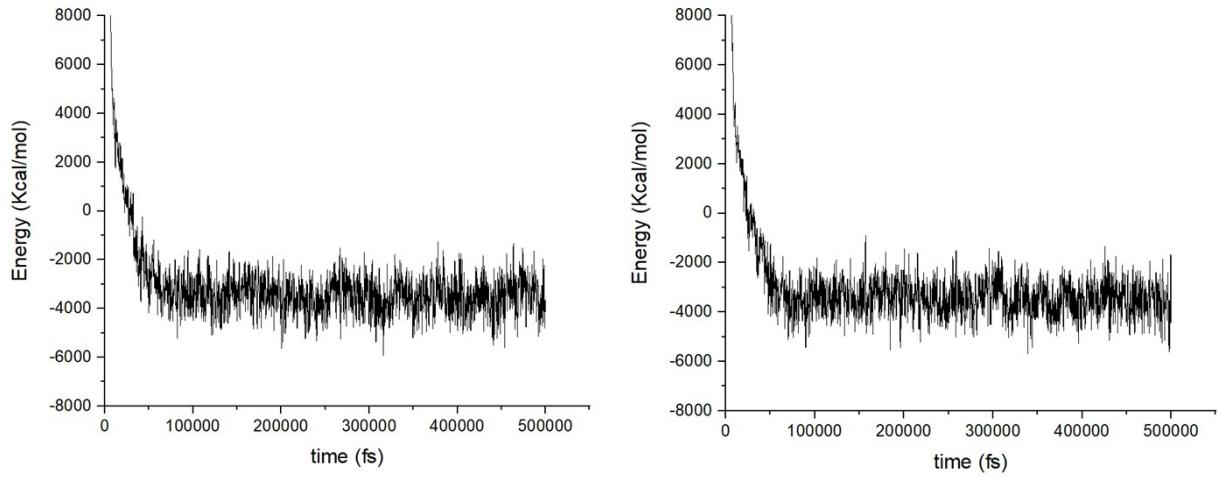


Fig. S1. Averaged energy (in kcal/mol) of simulation systems; (a) infinitely diluted benzene in CO2 and 2% Brine (4 wt.%), (b) infinitely diluted benzene in CO2 and 5% Brine (4 wt.%), (c) infinitely diluted benzene in CO2 and pure water (4 wt.%), (d) infinitely diluted pentane in CO2 and 2% Brine (4 wt.%), (b) infinitely diluted pentane in CO2 and 5% Brine (4 wt.%), (c) infinitely diluted pentane in CO2 and pure water (4 wt.%),

Intermolecular Potentials

Table S1. Parameters related to the solute (hydrocarbon: benzene and pentane)[1-3].

Molecule	Atom	Charge	σ (Å)	ε (kcal mol^{-1})	r (Å)	θ (deg)	Cn(C-C-C-C) (kcal mol^{-1})	Cn(H-C-C-X) (kcal mol^{-1})
Pentane	C_{CH2}	-0.148	3.5	0.066	$r_{(C-C)}$=1.529	$\theta_{(C-C-C)}$=112.7	C_0=0.123993	C_0=0.15
	H_{CH2}	0.074	2.5	0.0263	$r_{(C-H)}$=1.09	$\theta_{(C-C-H)}$=110.7	C_1=-0.05501	C_1=0.45
	C_{CH3}	-0.222	3.5	0.066		$\theta_{(H-C-H)}$=107.8	C_2=0.214342	C_2=0
	H_{CH3}	0.074	2.5	0.03			C_3=-0.35643	C_3=-0.6
Benzene	C	-0.115	3.55	0.07	$r_{(C-C)}$=1.40	$\theta_{(C-C-C)}$=120		
	H	0.115	2.42	0.03	$r_{(C-H)}$=1.08	$\theta_{(C-C-H)}$=120		

Table S2. Parameters related to the solution (CO_2, water and salt)[4-6].

Molecules	Atoms/Ions	q (e)	σ (Å)	ε (Kcal/mol)	r_{O-H}	$\theta_{H=O=H}$
H_2O	O	-1.1128	3.1589	0.1852	0.9572	104.52°
	H	0.5564	0.0	0.0		
Molecules	Atoms/Ions	q (e)	σ (Å)	ε (Kcal/mol)	$r_{C=O}$	$\theta_{O=C=O}$
CO_2	C	0.6512	2.757	0.0558	1.149	180°
	O	-0.3256	3.033	0.1599		
Molecules	Atoms/Ions	q (e)	σ (Å)	ε (Kcal/mol)		
Salt	Na^{1+}	1.00	2.35	0.13		
	Cl^{1-}	-1.00	4.40	0.10		

References

(1) L. Jorgensen, W.; S. Maxwell, D.; Tirado-Rives, J. Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids. J. Am. Chem. Soc. 1996, 118 (45), 11225–11236. https://doi.org/10.1021/ja9621760.

(2) Kaminski, G. A.; Friesner, R. A.; Tirado-Rives, J.; Jorgensen, W. L. Evaluation and Reparametrization of the OPLS-AA Force Field for Proteins via Comparison with Accurate Quantum Chemical Calculations on Peptides. J. Phys. Chem. B 2001, 105 (28), 6474–6487. https://doi.org/10.1021/jp003919d.

(3) Siu, S. W. I.; Pluhackova, K.; Böckmann, R. A. Optimization of the OPLS-AA Force Field for Long Hydrocarbons. J. Chem. Theory Comput. 2012, 8 (4), 1459–1470. https://doi.org/10.1021/ct200908r.

(4) Abascal, J. L. F.; Vega, C. A General Purpose Model for the Condensed Phases of Water: TIP4P/2005. J. Chem. Phys. 2005, 123 (23), 234505. https://doi.org/10.1063/1.2121687.

(5) Harris, J. G.; Yung, K. H. Carbon Dioxide's Liquid-Vapor Coexistence Curve And Critical Properties as Predicted by a Simple Molecular Model. J. Phys. Chem. 1995, 99 (31), 12021–12024. https://doi.org/10.1021/j100031a034.

(6) Smith, D. E.; Dang, L. X. Computer Simulations of NaCl Association in Polarizable Water. J. Chem. Phys. 1994, 100 (5), 3757–3766. https://doi.org/10.1063/1.466363.