Atomistic Molecular Dynamics Simulations of Carbon Dioxide Diffusivity in *n*-Hexane, *n*-Decane, *n*-Hexadecane, Cyclohexane and Squalane

Supporting information

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Table S1. Force field parameters for the hydrocarbons examined in this study.

	OPLS-AA[1]	L-OPLS[2]
$r_{0_{C-C}}$ (Å)	1.529	
$k_{r_{C-C}}$ (kcal mol⁻¹ Å⁻²)	536	
$r_{0_{C-H}}$ (Å)	1.09	
$k_{r_{C-H}}$ (kcal mol⁻¹ Å⁻²)	680	-
$\theta_{0_{C-C-C}}$ (deg)	112.7	
$k_{\theta_{C-C-C}}$ (kcal mol⁻¹ rad⁻²)	116.7	
$\theta_{0_{C-C-H}}$ (deg)	110.7	
$k_{\theta_{C-C-H}}$ (kcal mol⁻¹ rad⁻²)	75	
$\theta_{0_{H-C-H}}$ (deg)	107.8	
$k_{\theta_{H-C-H}}$ (kcal mol⁻¹ rad⁻²)	66	
c_n (H − C − C − X)[a,b] (kcal mol⁻¹)	$c_0 = 0.15$; $c_1 = 0.45$; $c_2 = 0$; $c_3 = -0.6$	
c_n (C − C − C − C) (kcal mol⁻¹)	$c_0 = 0.7$; $c_1 = -0.35$; $c_2 = 0.05$; $c_3 = -0.4$	$c_0 = 0.123993$; $c_1 = -0.055017$; $c_2 = 0.2143420$; $c_3 = -0.356439$
ε_C (kcal mol⁻¹)	$\varepsilon_{C_{CH_3}} = \varepsilon_{C_{CH_2}} = 0.066$; $\varepsilon_{C_{CH}} = 0.076$	
ε_H (kcal mol⁻¹)	$\varepsilon_{C_{CH_3}} = \varepsilon_{H_{CH}} = 0.03$; $\varepsilon_{H_{CH_2}} = 0.03$	$\varepsilon_{H_{CH_2}} = 0.0263$
σ_C (Å)	$\sigma_{C_{CH_3}} = \sigma_{C_{CH_2}} = 3.5$; $\sigma_{C_{CH}} = 3.55$	
σ_H (Å)	$\sigma_{H_{CH_3}} = \sigma_{H_{CH_2}} = 2.5$; $\sigma_{H_{CH}} = 2.42$	
q_C (e)	$q_{C_{CH_3}} = -0.18$; $q_{C_{CH_2}} = -0.12$; $q_{C_{CH}} = -0.06$	$q_{C_{CH_3}} = -0.222$; $q_{C_{CH_2}} = -0.148$; $q_{C_{CH}} = -0.160$
q_H (e)	$q_H = 0.06$	$q_{H_{CH_3}} = q_{H_{CH_2}} = 0.074$; $q_{H_{CH}} = 0.160$

	TraPPE-UA[3]
r_{C-C} (Å)	1.54
$\theta_{0_{C-C-C}}$ (deg)	114
$k_{\theta_{C-C-C}}$ (kcal mol⁻¹ rad⁻²)	124.2
$\theta_{0_{C-C-H}}$ (deg)	114
$k_{\theta_{C-C-H}}$ (kcal mol⁻¹ rad⁻²)	124.2
$\theta_{0_{H-C-H}}$ (deg)	114
$k_{\theta_{H-C-H}}$ (kcal mol⁻¹ rad⁻²)	124.2
c_n (C − C − C − C) (kcal mol⁻¹) n-alkanes	$c_0 = 2.007028$; $c_1 = -0.705521$; $c_2 = 0.271016$; $c_3 = -6.290094$
c_n (C − C − C − C) (kcal mol⁻¹) cyclohexane	$c_0 = 3.107959$; $c_1 = 13.21678$; $c_2 = 13.9364$; $c_3 = 0.500717$
c_n $\left(C_{CH_y} - C_{CH} - C_{CH_2} - C_{CH_2}\right)$[c] (kcal mol⁻¹) squalane	$c_0 = 0.785418$; $c_1 = -3.482664$; $c_2 = 0.444535$; $c_3 = 3.507553$
c_n $\left(C_{CH_z} - C_{CH_2} - C_{CH_2} - C_{CH_k}\right)$[d] (kcal mol⁻¹) squalane	$c_0 = 2.007004$; $c_1 = -5.423026$; $c_2 = 0.271013$; $c_3 = 6.290018$
ε (kcal mol⁻¹)	$\varepsilon_{CH_3} = 0.195$; $\varepsilon_{CH_2} = 0.0914$
σ (Å)	$\sigma_{CH_3} = = 3.75$; $\sigma_{CH_2} = = 3.95$

[a]For all torsions $c_4 = c_5 = 0$. [b]X is either a C or H atom. [c]y is either 2 or 3. [d]z and k are either 1 or 2.

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Table S2. Force field parameters for TraPPE-UA CO_2.

	TraPPE-UA[4]
r_{C-O} (Å)	1.16
θ_{O-C-O} (deg)	180
ε_C ($kcal\ mol^{-1}$)	0.0537
ε_O ($kcal\ mol^{-1}$)	0.157
σ_C (Å)	2.8
σ_O (Å)	3.05
q_C (e)	0.7
q_O (e)	-0.35

Table S3. Composition and box size lengths for the simulations of diffusion coefficient of CO_2 in the hydrocarbons.

	T (K)	P (MPa)	TraPPE			OPLS			L-OPLS		
			$N_{solvent}$	N_{solute}	box size (nm)	$N_{solvent}$	N_{solute}	box size (nm)	$N_{solvent}$	N_{solute}	box size (nm)
n-hexane		1	1000	5	6.024	300	3	4.034	300	3	4.038
	298.15	30	1000	5	5.932	300	3	3.982	300	3	3.988
		65	1000	5	5.859	300	3	3.939	300	3	3.940
		1	1000	5	6.096	300	3	4.089	300	3	4.100
	323.15	30	1000	5	5.985	300	3	4.024	300	3	4.030
		65	1000	5	5.901	300	3	3.976	300	3	3.976
		1	1000	5	6.534	300	3	4.430	300	3	4.467
	423.15	30	1000	5	6.227	300	3	4.217	300	3	4.227
		65	1000	5	5.915	300	3	4.124	300	3	4.126
n-decane		1	1000	5	6.900	300	3	4.596	300	3	4.609
	298.15	30	1000	5	6.816	300	3	4.555	300	3	4.569
		65	1000	5	6.748	300	3	4.512	300	3	4.531
		1	1000	5	6.965	300	3	4.645	300	3	4.659
	323.15	30	1000	5	6.869	300	3	4.598	300	3	4.609
		65	1000	5	6.789	300	3	4.557	300	3	4.567
		1	1000	5	7.292	300	3	4.895	300	3	4.898
	423.15	30	1000	5	7.089	300	3	4.780	300	3	4.784
		65	1000	5	6.959	300	3	4.704	300	3	4.708
n-hexadecane		1	1000	5	7.836	300	3	5.064	300	3	5.274
	298.15	30	1000	5	7.770	300	3	5.062	300	3	5.232
		65	1000	5	7.710	300	3	5.032	300	3	5.195
		1	1000	5	7.894	300	3	5.096	300	3	5.321
	323.15	30	1000	5	7.823	300	3	5.078	300	3	5.277
		65	1000	5	7.754	300	3	5.060	300	3	5.241
		1	1000	5	8.154	300	3	5.419	300	3	5.541
	423.15	30	1000	5	8.025	300	3	5.247	300	3	5.453
		65	1000	5	7.921	300	3	5.206	300	3	5.384
cyclohexane		1	1000	5	5.647	300	3	3.787			
	298.15	30	1000	5	5.585	300	3	3.753			
		65	1000	5	5.531	300	3	3.722			
		1	1000	5	5.701	300	3	3.835			
	323.15	30	1000	5	5.632	300	3	3.793			
		65	1000	5	5.569	300	3	3.755			
		1	1000	5	5.992	300	3	4.092			
	423.15	30	1000	5	5.830	300	3	3.967			
		65	1000	5	5.726	300	3	3.890			

squalane		1	300	3	6.405	300	3	6.343
	298.15	30	300	3	6.356	300	3	6.310
		65	300	3	6.310	300	3	6.283
		1	300	3	6.443	300	3	6.395
	323.15	30	300	3	6.390	300	3	6.356
		65	300	3	6.335	300	3	6.320
		1	300	3	6.616	300	3	6.616
	423.15	30	300	3	6.527	300	3	6.542
		65	300	3	6.451	300	3	6.479
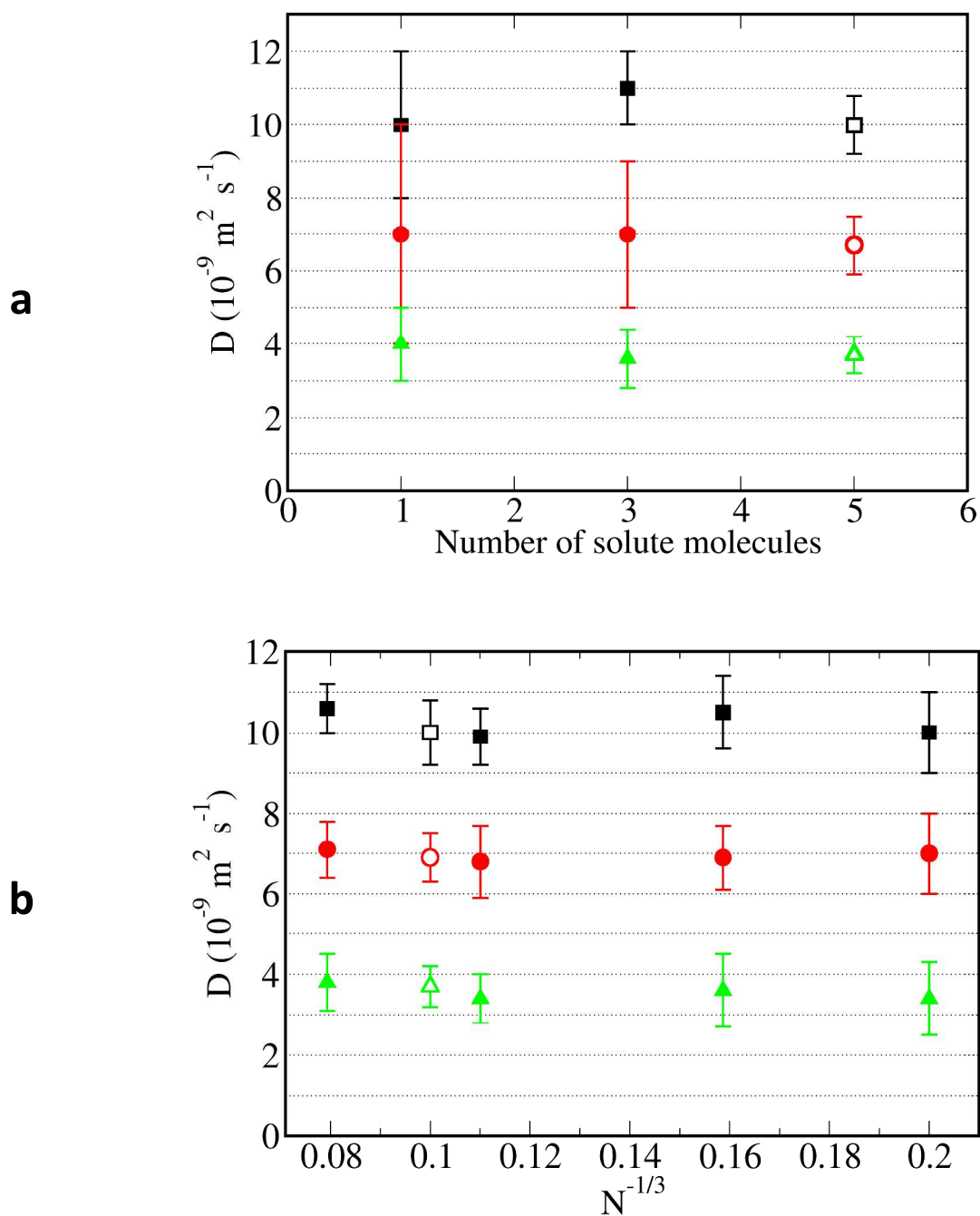
Figure S1. Diffusion coefficient of CO_2 in *n*-hexane (black squares), *n*-decane (red circles) and *n*-hexadecane (green triangles) with TraPPE force field, at 298.15 K and 1 MPa, as a function of (a) the number of solute molecules and (b) the number of solvent molecules. Open symbols correspond to the system sizes used in this study for TraPPE *n*-alkanes.
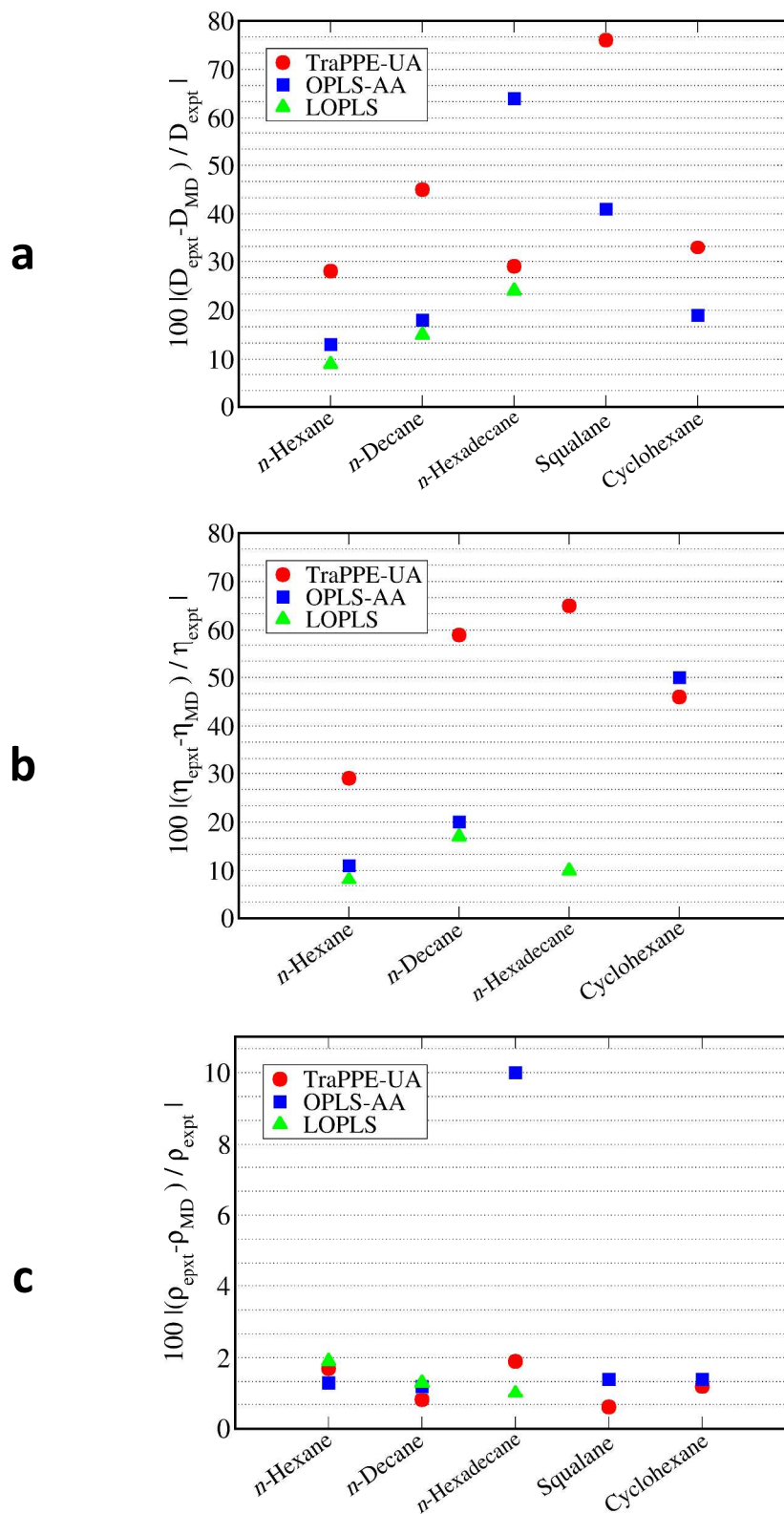
Figure S2. Percentage average absolute deviation of calculated values for (a) Diffusion coefficient of CO_2 in hydrocarbons, (b) Viscosity and (c) Density of *n*-hexane, *n*-decane, *n*-hexadecane, cyclohexane and squalane from experimental data.

Cadogan et al.[5] correlated the diffusion coefficient values of CO_2 in the hydrocarbons using the rough-hard-sphere theory. The authors found that the correlation describes the data very accurately within a range of $1.3 < V_m/V_0 < 2.0$, where V_m is the molar volume and V_0 the closed-packed molar volume of the solvent. In a similar fashion to the experimental study, we examined the dependence of CO_2 diffusivity in the various hydrocarbons on the molar volume of the hydrocarbon, obtained by each force field. In Figure S3, $D_{CO_2}T^{-0.5}$ is plotted as a function of the molar volume, V_m, for the three linear hydrocarbons, for all the force fields examined. Linear behavior is observed for the majority of cases ($R^2 \geq 0.98$), in good agreement with the experimental measurements, also shown. In Figure S4, the same correlation is shown for the cases of cyclohexane and squalane. The behavior is very similar to the linear ones.
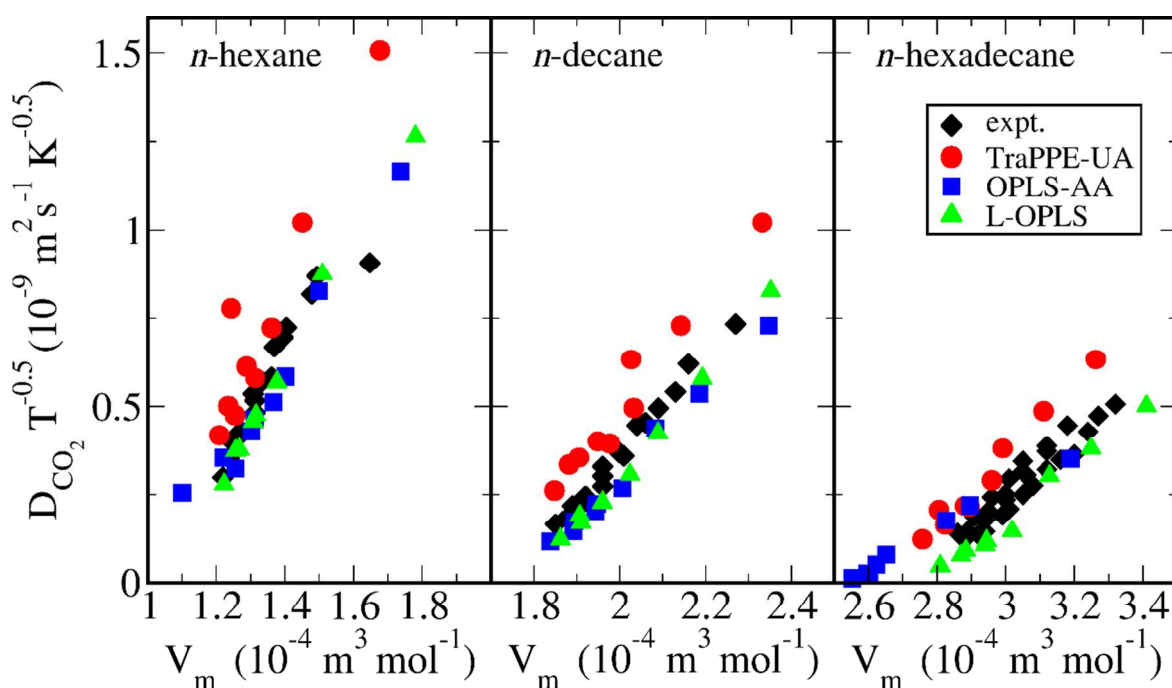

Figure S3. $D_{CO_2}T^{-0.5}$ of CO_2 in n-hexane (left), n-decane (middle) and n-hexadecane (right) as a function of the molar volume of the solvent. Experimental measurements are from Cadogan et al.[5]
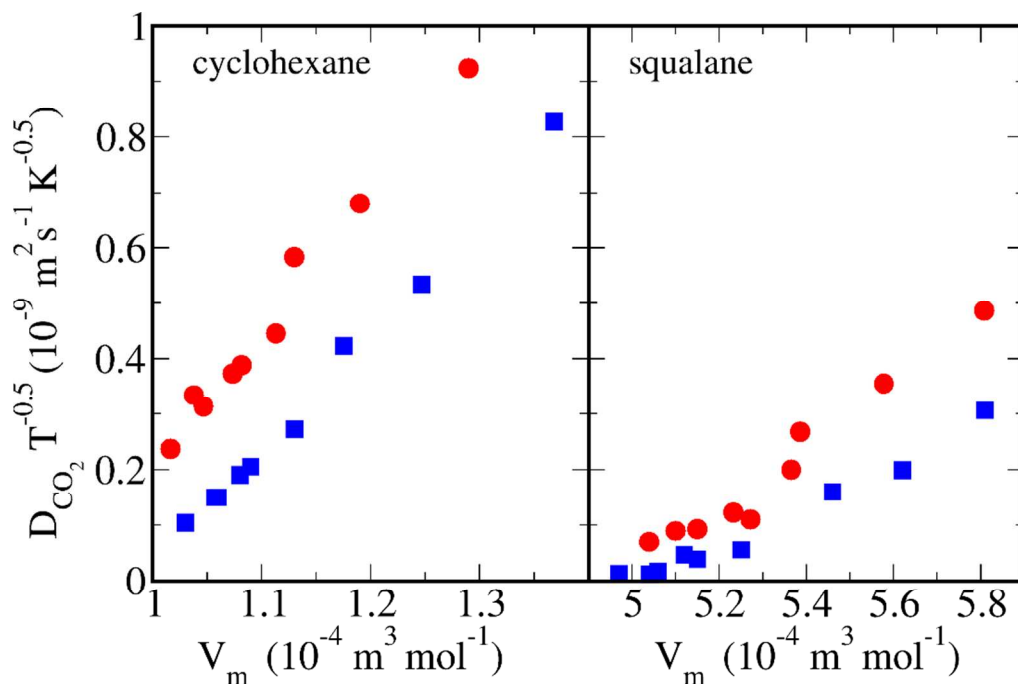
Figure S4. $D_{CO_2}T^{-0.5}$ of CO_2 in cyclohexane (left) and squalane (right) as a function of the molar volume of the solvent. Symbols are the same as in Figure S3. For the case of squalane there are deviations from linearity at lower molar volumes for both force fields, which is consistent with the experimental observations.[5]

References

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