Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Interfacial Anomaly in Low Global Warming Potential Refrigerant Blends as Predicted by Molecular Dynamics Simulations

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Table 1. Force field parameters used for HFO-1234yf, HFO-1234ze (E) and HC-600a

	Force	Force Constant		REF
	Atom Types	ε (kcal/mol)	σ (Å)	
HFO-1234yf	FCT	0.056	2.94	[1]
	FCM	0.056	2.9	
	CT	0.074	3.4	
	CM	0.098	3.4	
	HC	0.016	2.65	
	H1	0.016	2.47	
HFO-1234ze (E)	FCT	0.05645	2.94	[2]
	FCM	0.05645	2.9	
	CT	0.07431	3.4	
	CM	0.09799	3.4	
	HC	0.0157	2.65	
	H1	0.0157	2.47	
HC-600a	CT	0.066	3.5	[3]
	HC	0.03	2.5	
	Bond	k_r (kcal/(mol·Å^2))	r_0 (Å)	
HFO-1234yf	CM=CM	676.79	1.331	[1]
	CM-CT	317.6	1.511	
	CT-FCT	369.17	1.353	
	CM-HC	388.88	1.086	
	CM-FCM	445.68	1.33	
HFO-1234ze (E)	FCT-CT	369.17065	1.353	[2]
	FCM-CM	445.68117	1.33	
	CT-CM	317.60038	1.511	

	CM=CM	676.79015	1.331	
	CM-HC/H1	388.87906	1.086	
HC-600a	CT-CT	268	1.529	[3]
	CT-HC	340	1.09	
	Angle	k_θ (kcal/(mol·rad^2))	θ_0 (deg)	
HFO-1234yf	HC-CM=CM	36.35	120.6	[1]
	FCT-CT-FCT	87.86	107.5	
	CM-CT-FCT	74.85	111.3	
	HC-CM-HC	29.31	118.7	
	CM=CM-FCM	50.52	122.6	
	FCM-CM-CT	76.38	112.5	
	CM=CM-CT	50.12	124.1	
HFO-1234ze (E)	FCT-CT-FCT	87.861	107.5	[2]
	FCT-CT-CM	74.84951	111.3	
	CT-CM=CM	50.1195	124.1	
	CT-CM-HC	32.33034	115.1	
	CM=CM-HC	36.35042	120.6	
	FCM-CM=CM	50.52109	122.6	
	FCM-CM-H1	51.23333	113.7	
HC-600a	CT-CT-HC	37.5	110.7	[3]
	HC-CT-HC	33	107.8	

Table 2. Force field parameters used for the dihedral potential of HFO-1234yf, HFO-1234ze (E)

	Dihedral	k_x	n	σ (deg)	REF
HFO-1234yf	FCT-CT-CM-FCM	0.25	3	0	[1]
	FCT-CT-CM=CM	0.14	3	180	
	FCM-CM=CM-HC	6.65	2	180	
	CT-CM=CM-HC	6.65	2	180	
	FCM-CM=CM-HC	6.65	1	180	
	HC-CM=CM-H1	6.65	1	0	
HFO-1234ze (E)	FCT-CT-CM=CM	0.14223	3	0	[2]
	FCT-CT-CM-HC	0.17806	3	180	
	FCM-CM=CM-CT	6.65392	1	180	
	CT-CM=CM-H1	6.65392	1	0	
	FCM-CM=CM-HC	6.65392	1	180	
	HC-CM=CM-H1	6.65392	1	0	

Table 3. Force field parameters used in this work for the dihedral potential of HC-600a

	Dihedral	K1	K2	K3	K4	REF
HC-600a	CT-CT-CT-HC	0	0	0.366	0	[3]
	HC-CT-CT-HC	0	0	0.318	0	

Table 4. Partial Charges of HFO-1234yf and HFO-1234ze (E) used in this work [3]

HFO-1234yf		HFO-1234ze (E)	
Type	*q (e)*	Type	*q (e)*
FCT	-0.212	FCT	-0.24329
FCM	-0.1825	FCM	-0.19161
CT	0.6306	CT	0.77614
CM	0.1974	CM	-0.48504
CM	-0.4191	CM	0.25325
HC	0.2048	HC	0.24464
HC	0.2048	HC	0.13249

Table 5. MD simulation results of pure HFO-1234yf: saturated densities, surface tension and interface thickness, with their corresponding standard deviation (SD).

T/K	ρ_l/kg·m^{-3}	ρ_g/kg·m^{-3}	γ /mN·m^{-1}	d/Å
253.15	1235.8±2.2	6.5±1.2	11.61±0.09	6.21±0.07
263.15	1203.6±2.7	10.6±0.6	10.7±0.3	4.91±0.02
273.15	1174.2±1.9	20.1±0.5	8.9±0.2	5.42±0.03
283.15	1134.0±1.1	28.0±0.6	7.7±0.1	5.97±0.04
293.15	1096.7±2.9	34.3±0.5	6.9±0.4	6.55±0.05
303.15	1059.6±1.2	39.2±0.7	5.9±0.2	7.14±0.05
313.15	1023.1±1.9	62.8±0.7	4.5±0.1	8.99±0.07
323.15	966.2±1.5	72.9±0.8	3.5±0.2	10.71±0.09
333.15	918.7±2.0	96.4±1.1	2.6±0.2	12.4±0.1
343.15	880.5±1.9	125.7±1.0	1.6±0.3	13.5±0.1

Table 6. MD simulation results of pure HFO-1234ze (E): saturated densities, surface tension and interface thickness, with their corresponding standard deviation (SD).

T/K	ρ_l/kg·m^{-3}	ρ_g/kg·m^{-3}	γ /mN·m^{-1}	d(Å)
253.15	1311.44±1.1	6.3±0.5	14.15±0.05	3.83±0.02
263.15	1288.8±1.7	8.5±0.7	12.87±0.07	5.82±0.04
273.15	1246.67±1.4	12.0±0.4	11.6±0.2	6.40±0.05
283.15	1234.9±2.0	16.5±0.8	9.9±0.3	7.07±0.05
293.15	1175.0±1.6	28.7±0.6	9.1±0.1	7.69±0.02
303.15	1150.6±2.2	33.6±0.8	8.1±0.2	8.38±0.06
313.15	1104.1±2.4	50.0±0.1	6.5±0.1	8.63±0.04
323.15	1071.1±1.5	55.5±0.5	5.9±0.2	8.84±0.05
333.15	1033.2±3.4	80.2±1.2	4.3±0.1	8.92±0.07
343.15	963.6±8.2	102.9±2.6	3.4±0.1	9.2±0.3

Table 7. MD simulation results of pure HC-600a: saturated densities, surface tension and interface thickness, with their corresponding standard deviation (SD).

T/K	ρ_l/kg·m^{-3}	ρ_g/kg·m^{-3}	γ /mN·m^{-1}	d(Å)
253.15	617.5±0.4	2.4±0.3	15.0±0.2	5.05±0.02
263.15	610.1±0.5	3.8±0.3	14.2±0.5	5.19±0.03
273.15	587.1±0.6	6.5±0.6	12.6±0.2	5.35±0.02
283.15	579.2±0.5	7.6±0.4	11.5±0.4	5.64±0.06
293.15	565.4±0.3	8.9±0.3	10.4±0.4	5.72±0.02
303.15	552.4±0.5	14.6±0.3	9.5±0.3	5.81±0.04
313.15	531.9±0.3	19.7±0.6	8.5±0.4	7.02±0.03
323.15	517.1±0.3	24.5±0.4	7.2±0.1	8.13±0.05
333.15	501.4±0.5	25.2±0.3	6.4±0.3	9.44±0.05

Table 8. MD simulation results for the binary mixture HFO-1234yf +HC-600a: liquid mole fractions of HC-600a (x_1), vapor mole fractions of HC-600a (y_1), vapor pressure (P), surface tension (γ) and their corresponding standard derivation (SD) at different temperatures and different initial compositions (HC-600a) in the simulation box.

	Initial composition HC	x_1	y_1	P(MPa)	γ (mN/m)
283.15K	0	0	0	0.44±0.07	7.73±0.08
	0.1	0.0991	0.0909	0.44±0.01	7.6±0.1
	0.14	0.0984	0.0952	0.45±0.04	7.6±0.3
	0.3	0.326	0.156	0.44±0.04	8.0±0.4
	0.5	0.483	0.351	0.42±0.03	8.7±0.1
	0.7	0.725	0.565	0.4±0.1	9.4±0.3
	0.9	0.912	0.737	0.29±0.02	10.6±0.6
	1	1	1	0.22±0.03	11.5±0.2
293.15K	0	0	0.140	0.59±0.05	6.9±0.1
	0.1	0.0970	0.138	0.60±0.03	6.8±0.1
	0.3	0.297	0.336	0.59±0.06	7.9±0.2
	0.5	0.512	0.408	0.56±0.03	8.6±0.3
	0.7	0.785	0.655	0.5±0.1	8.1±0.6
	0.9	0.970	0.913	0.3±0.1	9.3±0.7
	1	1	1	0.31±0.01	10.37±0.09

Table 9. MD simulation results for the binary mixture HFO-1234ze (E) + HC-600a: liquid mole fractions of HC-600a (x_1), vapor mole fractions of HC-600a (y_1), vapor pressure (P), surface tension (γ) and their corresponding standard derivation (SD) at different temperatures and different initial compositions (HC-600a) in the simulation box.

	Initial composition HC	x_1	y_1	P (MPa)	γ (mN/m)
268.15K	0	0	0	0.18±0.02	12.79±0.09
	0.1	0.0939	0.0131	0.19±0.02	12.4±0.4
	0.3	0.294	0.403	0.21±0.04	11.7±0.3
	0.455	0.451	0.448	0.21±0.02	11.6±0.1
	0.7	0.715	0.494	0.20±0.03	11.8±0.2
	0.9	0.912	0.668	0.17±0.04	12.5±0.6
	1	1	1	0.13±0.01	12.98±0.07
288.15K	0	0	0	0.37±0.03	10.1±0.1
	0.1	0.0990	0.112	0.39±0.02	9.6±0.4
	0.3	0.295	0.348	0.46±0.02	9.2±0.2
	0.408	0.405	0.413	0.41±0.01	9.1±0.2
	0.7	0.715	0.562	0.38±0.02	9.7±0.5
	0.9	0.903	0.837	0.32±0.04	10.48±0.8
	1	1	1	0.26±0.03	11.1±0.2

References

[1] G. Raabe and E. J. Maginn, "A force field for 3, 3, 3-fluoro-1-propenes, including HFO-1234yf," *The Journal of Physical Chemistry B,* vol. 114, pp. 10133-10142, 2010.

[2] G. Raabe, "Molecular modeling of fluoropropene refrigerants," *The Journal of Physical Chemistry B,* vol. 116, pp. 5744-5751, 2012.

[3] W. L. Jorgensen, D. S. Maxwell, and J. Tirado-Rives, "Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids," *Journal of the American Chemical Society,* vol. 118, pp. 11225-11236, 1996/01/01 1996.