



SUPPLEMENTARY MATERIAL TO
**Correlation of the solubility of solid hydrocarbons in
supercritical CO₂ using different equations of state
and mixing rules**

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The constants of PR and SRK equations of state are as below:

For SRK equation of state, $c_1=0$ and $c_2=1$.

$$a = a_c \left[1 + m \left(1 - \sqrt{T_r} \right) \right]^2 \quad (\text{S-1})$$

$$a_c = 0.42748 \frac{R^2 T_c^2}{P_c} \quad (\text{S-2})$$

$$m = 0.48 + 1.574\omega - 0.176\omega^2 \quad (\text{S-3})$$

$$b = 0.08664 \frac{RT_c}{P_c} \quad (\text{S-4})$$

where, T_c , P_c and ω are indicative of critical temperature, critical pressure and acentric factor. T_r and R are the reduced temperature and universal gas constant. Similarly, for the PR equation of state, $c_1=1-2^{1/2}$ and $c_2=1+2^{1/2}$.

$$a = a_c \left[1 + m \left(1 - \sqrt{T_r} \right) \right]^2 \quad (\text{S-5})$$

$$a_c = 0.45724 \frac{R^2 T_c^2}{P_c} \quad (\text{S-6})$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (\text{S-7})$$

$$b = 0.007780 \frac{RT_c}{P_c} \quad (\text{S-8})$$

For a mixture of heavy component and SCF, the EOS parameters a and b are calculated by the following mixing rules:¹

vdW1 mixing rule:

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$$a = \sum_i \sum_j y_i y_j a_{ij} \quad (\text{S-9})$$

$$b = \sum_j y_j b_j \quad (\text{S-10})$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (\text{S-11})$$

vdW2 mixing rule:

$$a = \sum_i \sum_j y_i y_j a_{ij} \quad (\text{S-12})$$

$$b = \sum_i \sum_j y_i y_j b_{ij} \quad (\text{S-13})$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (\text{S-14})$$

$$b_{ij} = \frac{b_i + b_j}{2} (1 - l_{ij}) \quad (\text{S-15})$$

CVD mixing rule:

$$a = \sum_i \sum_j y_i y_j a_{ij} \left(\frac{b}{b_{ij}} \right)^{M_{ij}} \quad (\text{S-16})$$

$$b = \sum_j y_j b_j \quad (\text{S-17})$$

$$a_{ij} = \sqrt{a_i a_j} \quad (\text{S-18})$$

$$b_{ij} = \sqrt{b_i b_j} \quad (\text{S-19})$$

Where, y_i and y_j are the mole fractions of the components i and j , and k_{ij} and l_{ij} are the binary interaction parameters, and i and j refer to i^{th} and j^{th} compound in the mixture. M_{ij} indicates the adjustable parameter in the CVD mixing rule. \hat{a}_i and \hat{b}_i in equation (7) of the manuscript are derivatives related to the attractive and repulsive parameters of EOS, which are calculated from the following equations:

vdW1 mixing rule:

$$\hat{a}_i = \left[\frac{\partial (na)}{\partial n_i} \right]_{T,P,n_{j \neq i}} = 2 \sum_{j=1}^N y_j a_{ij} \quad (\text{S-20})$$

$$\hat{b}_i = \left[\frac{\partial (nb)}{\partial n_i} \right]_{T,P,n_{j \neq i}} = b_i \quad (\text{S-21})$$

vdW2 mixing rule:

$$\hat{a}_i = \left[\frac{\partial(na)}{\partial n_i} \right]_{T,P,n_{j \neq i}} = 2 \sum_{j=1}^N y_j a_{ij} \quad (\text{S-22})$$

$$\hat{b}_i = \left[\frac{\partial(nb)}{\partial n_i} \right]_{T,P,n_{j \neq i}} = 2 \sum_{j=1}^N y_j b_{ij} \quad (\text{S-23})$$

CVD mixing rule:

$$\hat{a}_i = \left[\frac{\partial(na)}{\partial n_i} \right]_{T,P,n_{j \neq i}} = 2 \sum_{j=1}^N \left(y_j a_{ji} \left(\frac{b}{b_{ij}} \right)^{M_{ij}} \right) + \left(\frac{b_i}{b} - 1 \right) \left[\sum_i \sum_j y_i y_j a_{ij} M_{ij} \left(\frac{b}{b_{ij}} \right)^{M_{ij}} \right] \quad (\text{S-24})$$

$$\hat{b}_i = \left[\frac{\partial(nb)}{\partial n_i} \right]_{T,P,n_{j \neq i}} = b_i \quad (\text{S-25})$$

The fitted binary parameters for modeling results and AARD for the combination of PR or SRK EoS and three mixing rules are given for 1-hexadecanol, 1-octadecanol, anthracene, benzoin, fluorene, hexamethylbenzene, mandelic acid, naphthalene, palmitic acid, phenanthrene, propyl 4-hydroxybenzoate, pyrene and stearic acid at different pressures and temperatures in Table S-I for calculation of solubility of heavy compounds in supercritical CO₂.

TABLE S-I. AARD for the solubility of pure component in supercritical CO₂ with the combination of three mixing rules and the PR and SRK EoS and optimized values of the binary interaction parameters (k_{ij} , l_{ij} and M_{ij}) for these EoS's

Component: 1-Hexadecanol						
T / K	Pressure range, bar	Number of points	Ref.	EoS	Mixing rule: vdW1	
					k_{ij}	AARD
318.1	52.1-415.1	7	15	PR	0.01587	48.906
				SRK	0.20536	51.786
328.15	141.8-415.9	5	15	PR	0.04241	14.342
				SRK	0.05924	15.202
338.15	147.1-373	6	15	PR	0.08148	82.776
				SRK	0.09667	86.544
Component: 1-Hexadecanol						
T / K	Pressure range, bar	Mixing rule: vdW2			Mixing rule: CVD	
		k_{ij}	l_{ij}	AARD	M_{ij}	AARD
318.1	52.1-415.1	0.01572	0.09993	12.271	0.84757	55.306
		0.15127	0.25232	15.270	0.89164	55.306
328.15	141.8-415.9	0.04209	0.06995	13.290	0.85462	50.206
		0.06198	0.09457	13.416	0.87767	52.505
338.1	147.1-373	0.08308	0.15000	10.780	0.98826	100.204
		0.14340	0.17999	11.032	0.91475	105.040
Component: 1-Octadecanol						
T / K	Pressure range, bar	Number of points	Ref.	EoS	Mixing rule: vdW1	
					k_{ij}	AARD
318.1	152.437.9	4	16	PR	0.15736	8.756
				SRK	0.18064	10.970

328.1	139.9-447.7	7	16	PR	0.19985	69.686
				SRK	0.22394	72.450
338.1	145.8-452.8	6	16	PR	0.13451	70.238
				SRK	0.14392	74.256
Component: 1-Octadecanol						
T / K	Pressure range, bar	Mixing rule: vdW2			Mixing rule: CVD	
		k_{ij}	l_{ij}	AARD	M_{ij}	AARD
318.1	152.437.9	0.01604	0.05836	2.756	0.89275	10.044
		0.10013	0.13714	4.128	0.91746	14.206
328.1	139.9-447.7	0.13672	0.22387	7.128	0.93276	84.947
		0.14236	0.23713	11.239	0.97265	85.283
338.1	145.8-452.8	0.15219	0.21613	8.237	0.98735	88.385
		0.16513	0.21624	9.023	0.98725	80.039
Component: Anthracene						
T / K	Pressure range, bar	Number of points	Ref.	EoS	Mixing rule: vdW1	
					k_{ij}	AARD
303.1	104.3-414.5	4	24	PR	0.06689	14.106
				SRK	0.07081	22.321
308.0	104.3-276.7	5	17	PR	0.06627	27.724
				SRK	0.07145	31.244
308.1	120-350	6	18	PR	0.23268	6.294
				SRK	0.15031	8.859
313.1	100-200	7	19	PR	0.25591	7.764
				SRK	0.17976	10.071
318.1	104.3-276.7	6	17	PR	0.07212	14.413
				SRK	0.07588	13.584
323.1	90.6-414.5	10	24	PR	0.07064	23.709
				SRK	0.07116	30.354
343.1	118.1-414.5	9	24	PR	0.07226	12.258
				SRK	0.06983	13.430
Component: Anthracene						
T / K	Pressure range, bar	Mixing rule: vdW2			Mixing rule: CVD	
		k_{ij}	l_{ij}	AARD	M_{ij}	AARD
303.1	104.3-414.5	0.05597	89.99946	7.358	0.79824	16.310
		5.83E-02	84.99995	12.202	0.89274	15.320
308.0	104.3-276.7	0.05411	0.13341	26.105	0.76264	30.029
		0.05136	0.14497	27.607	0.79284	31.394
308.1	120-350	0.03878	0.07999	4.373	0.84463	7.020
		0.07346	1.99830	6.685	1.04595	11.800
313.1	100-200	0.04999	0.10454	4.401	0.86808	17.117
		0.09315	0.12673	9.229	1.12968	20.102
318.1	104.3-276.7	0.07639	0.09930	12.988	0.84728	15.094
		0.08054	0.11931	12.429	0.87163	14.292
323.1	90.6-414.5	0.05834	0.14067	20.872	0.91273	23.695
		0.05316	0.16772	25.762	0.88264	29.290
343.1	118.1-414.5	0.06244	0.14487	10.054	0.78216	13.395
		0.05683	0.16436	10.844	0.81738	15.204

Component: Benzoin						
T / K	Pressure range, bar	Number of points	Ref.	EoS	Mixing rule: vdW1	
					k_{ij}	AARD
308.1	121.6-236.1	6	25	PR	0.10237	5.317
				SRK	0.11717	5.915
318.15	111.3-241.9	7	25	PR	0.11718	6.383
				SRK	0.09175	6.014
328.1	114.8-244.3	6	25	PR	0.12747	8.264
				SRK	0.13473	7.276
Component: Benzoin						
T / K	Pressure range, bar	Mixing rule: vdW2			Mixing rule: CVD	
		k_{ij}	l_{ij}	AARD	M_{ij}	AARD
308.1	121.6-236.1	0.09372	0.16382	4.183	0.81265	6.024
		0.12175	0.15172	5.128	0.71636	6.847
318.1	111.3-241.9	0.10983	0.13286	5.185	0.87264	8.305
		0.08617	0.17648	3.836	0.83764	7.430
328.1	114.8-244.3	0.11364	0.16353	7.763	0.80373	10.295
		0.14524	0.15473	6.263	0.81646	9.205
Component: Fluorene						
T / K	Pressure range, bar	Number of points	Ref.	EoS	Mixing rule: vdW1	
					k_{ij}	AARD
303.1	83.6-483.5	7	24	PR	0.12918	12.481
				SRK	0.19448	18.104
308.1	83.7-414.5	6	24	PR	0.15221	15.929
				SRK	0.15728	24.671
308.2	78.3-203.5	47	21	PR	0.12756	10.473
				SRK	0.13139	10.986
308.2	83.6-483.4	7	24	PR	0.13105	12.054
				SRK	0.13889	14.129
313.1	100-200	5	19	PR	0.16936	6.369
				SRK	0.17854	7.827
318.2	85-254	21	21	PR	0.28537	10.477
				SRK	0.26448	12.685
323.15	69.9-414.5	9	24	PR	0.13858	25.059
				SRK	0.16692	29.287
343.1	104.3-483.4	7	24	PR	0.14536	27.494
				SRK	0.15939	30.209

Component: Fluorene						
<i>T</i> / K	Pressure range, bar	Mixing rule: vdW2			Mixing rule: CVD	
		k_{ij}	l_{ij}	AARD	M_{ij}	AARD
303.15	83.6-483.5	0.18373	0.20947	9.937	1.03837	15.303
		0.21045	0.28728	11.193	1.73734	20.294
308.15	83.7-414.5	0.15226	0.22999	7.394	0.99837	16.394
		0.15463	0.69999	20.439	1.02928	27.447
308.2	78.3-203.5	0.13819	0.19628	5.202	1.01038	11.233
		0.13574	0.20483	6.037	0.99783	19.304
308.2	83.6-483.4	0.15838	0.23950	8.938	1.03928	14.293
		0.14211	0.27985	10.392	1.01384	16.320
313.1	100-200	0.17837	0.21947	5.937	1.01923	7.029
		0.18476	0.22857	6.174	1.03284	8.393
318.2	85-254	0.15839	0.19583	9.094	1.07363	12.119
		0.16837	0.17483	11.449	1.04627	14.203
323.1	69.9-414.5	0.12958	0.14979	12.546	1.09237	35.303
		0.16097	0.20883	13.711	1.10498	37.202
343.1	104.3-483.4	0.13765	0.23834	12.093	1.09283	39.303
		0.14849	0.25829	13.059	0.99082	45.303
Component: Hexamethylbenzene						
<i>T</i> / K	Pressure range, bar	Number of points	Ref.	EoS	Mixing rule: vdW1	
					k_{ij}	AARD
303.1	69.9-345.6	7	24	PR	0.16938	9.984
				SRK	0.17839	10.203
308.15	150-350	4	19	PR	0.11849	10.048
				SRK	0.15927	14.593
323.1	69.9-345.6	10	24	PR	0.17470	12.049
				SRK	0.17462	13.208
343.1	83.7-483.5	10	24	PR	0.19284	10.446
				SRK	0.14828	13.588
Component: Hexamethylbenzene						
<i>T</i> / K	Pressure range, bar	Mixing Rule : vdW2			Mixing rule: CVD	
		k_{ij}	l_{ij}	AARD	M_{ij}	AARD
303.1	69.9-345.6	0.18746	0.18363	6.303	0.92736	10.084
		0.19283	0.21348	7.303	0.98165	11.918
308.1	150-350	0.20483	0.17366	5.483	1.01838	13.202
		0.26403	0.16362	7.302	0.99937	15.324
323.1	69.9-345.6	0.28472	0.19826	7.044	1.07374	14.203
		0.26173	0.20193	9.939	0.98326	16.125
343.1	83.7-483.5	0.21383	0.14726	11.434	0.98827	12.404
		0.23887	0.17646	11.381	1.0038	14.092
Component: Mandelic acid						
<i>T</i> / K	Pressure range, bar	Number of points	Ref.	EoS	Mixing rule: vdW1	
					k_{ij}	AARD
308.1	101-228.5	7	25	PR	0.07103	43.710
				SRK	0.07914	46.699
318.1	102.3-225.7	7	25	PR	0.07722	35.007
				SRK	0.08461	38.077
328.1	104.4-230.6	9	25	PR	0.07679	26.111
				SRK	0.08321	27.563

Component: Mandelic acid						
T / K	Pressure range, bar	Mixing Rule : vdW2			Mixing rule: CVD	
		k_{ij}	l_{ij}	AARD	M_{ij}	AARD
308.1	101-228.5	0.18347	0.41843	12.304	0.69294	57.303
		0.08035	0.37998	12.999	0.65123	60.202
318.1	102.3-225.7	0.17476	0.37592	14.437	0.68871	35.203
		0.08656	0.39999	13.059	0.69012	40.227
328.1	104.4-230.6	0.16832	0.41847	12.448	0.59283	33.203
		0.16482	0.43284	10.403	0.61385	32.403

Component: Naphthalene						
T / K	Pressure range, bar	Number of points	Ref.	EoS	Mixing rule: vdW1	
					k_{ij}	AARD
308.15	86.8-255.3	9	22	PR	0.09665	8.843
				SRK	0.09987	5.357
328.1	82.2-287.8	16	22	PR	0.09852	23.707
				SRK	0.09921	21.278
333.5	82.2-291.4	19	22	PR	0.10633	38.764
				SRK	0.10529	30.104
338.0	165-252.4	7	22	PR	0.11224	22.926
				SRK	0.11127	31.287

Component: Naphthalene						
T / K	Pressure range, bar	Mixing rule: vdW2			Mixing rule: CVD	
		k_{ij}	l_{ij}	AARD	M_{ij}	AARD
308.1	86.8-255.3	0.10868	0.49998	3.237	0.99272	9.101
		0.10679	0.25133	4.244	0.82826	7.494
328.1	82.2-287.8	0.00309	0.24324	11.385	0.82716	25.209
		0.02585	0.20343	7.491	0.84374	26.303
333.5	82.2-291.4	0.15622	0.18057	5.390	0.60929	41.304
		0.08823	0.25722	7.044	0.62847	45.339
338.0	165-252.4	0.07404	0.22484	2.786	0.78284	24.203
		0.082027	0.25373	3.539	0.7182	35.294

Component: Palmitic acid						
T / K	Pressure range, bar	Number of points	Ref.	EoS	Mixing rule: vdW1	
					k_{ij}	AARD
318.1	142.1-360.6	5	15	PR	0.04015	46.881
				SRK	0.06423	55.141
328.1	144.1-573.5	7	15	PR	0.03676	104.982
				SRK	0.06380	101.197
338.1	142.5-574.8	7	15	PR	0.04938	111.431
				SRK	0.07862	94.291

Component: Palmitic acid						
T / K	Pressure range, bar	Mixing rule: vdW2			Mixing rule: CVD	
		k_{ij}	l_{ij}	AARD	M_{ij}	AARD
318.15	142.1-360.6	0.01054	0.19484	34.311	0.76725	51.045
		0.04610	0.24637	36.403	0.79135	52.037
328.1	144.1-573.5	0.07827	0.15737	45.302	0.79274	110.04
		0.00793	0.16810	47.148	0.71546	113.504
338.1	142.5-574.8	0.05169	0.17383	35.492	0.82725	150.023
		0.09273	0.18393	37.428	0.87146	155.303

Component: Phenanthrene						
<i>T</i> / K	Pressure range, bar	Number of points	Ref.	EoS	Mixing rule: vdW1	
					k_{ij}	AARD
303.1	80.9-414.5	8	24	PR	0.11939	6.303
				SRK	0.13847	7.493
308.1	100-350	7	18	PR	0.12802	7.910
				SRK	0.13311	5.969
308.2	78.3-203.5	47	21	PR	0.13029	12.493
				SRK	0.12948	11.874
313.1	100-200	5	19	PR	0.11282	15.303
				SRK	0.10943	20.202
318.1	101-201	5	26	PR	0.12060	12.817
				SRK	0.12734	13.727
318.2	95-254	20	21	PR	0.09237	16.193
				SRK	0.13857	16.094
323.1	104.3-414.5	6	24	PR	0.13193	14.978
				SRK	0.13346	10.992
328.2	90-245	23	21	PR	0.09937	12.048
				SRK	0.12847	13.857
343.15	104.3-414.5	7	24	PR	0.13757	15.303
				SRK	0.14828	14.049
Component: Phenanthrene						
<i>T</i> / K	Pressure range, bar	Mixing rule: vdW2			Mixing rule: CVD	
		k_{ij}	l_{ij}	AARD	M_{ij}	AARD
303.1	80.9-414.5	0.13734	0.02857	6.304	1.01838	7.409
		0.16657	0.03827	7.000	1.12743	13.102
308.1	100-350	0.10240	0.07309	6.692	1.10348	18.912
		0.13357	0.16339	6.046	1.14257	14.385
308.2	78.3-203.5	0.19245	0.00002	10.019	0.93473	15.202
		0.20103	0.01833	11.303	0.94637	17.101
313.1	100-200	0.02938	0.38287	8.028	0.91636	20.202
		0.19373	0.01736	9.038	0.93727	22.371
318.15	101-201	0.14274	0.06999	6.992	1.10338	14.234
		0.12682	0.05727	13.724	1.21212	47.381
318.2	95-254	0.07173	0.02748	12.203	0.81636	18.202
		0.08273	0.01384	10.039	0.87463	17.209
323.1	104.3-414.5	0.10240	0.07309	6.692	1.10297	25.202
		0.12682	0.11938	9.652	1.39386	26.302
328.2	90-245	0.05663	-0.09983	8.0384	0.93874	18.503
		0.02348	0.18373	12.393	0.91837	17.493
343.1	104.3-414.5	0.07263	0.08726	12.394	0.82737	22.224
		0.07282	0.09826	13.928	0.82747	23.290

Component: Propyl 4-hydroxybenzoate						
T / K	Pressure range, bar	Number of points	Ref.	EoS	Mixing rule: vdW1	
					k_{ij}	AARD
308.15	94.1-220.9	7	25	PR	0.12737	10.2937
				SRK	0.14829	16.293
318.1	96.8-214.7	7	25	PR	0.15828	14.203
				SRK	0.12848	15.238
328.1	105.1-220.2	7	25	PR	0.15838	19.230
				SRK	0.17683	21.103
Component: Propyl 4-hydroxybenzoate						
T / K	Pressure range, bar	Mixing rule: vdW2			Mixing rule: CVD	
		k_{ij}	l_{ij}	AARD	M_{ij}	AARD
308.1	94.1-220.9	0.20193	0.19383	6.403	0.86253	15.204
		0.27467	0.17472	7.302	0.81543	14.204
318.1	96.8-214.7	0.21737	0.18237	9.129	0.79384	13.204
		0.21384	0.19438	10.39	0.81264	16.204
328.1	105.1-220.2	0.28577	0.20194	18.303	0.83727	22.405
		0.21747	0.17436	20.203	0.87464	26.304
Component: Pyrene						
T / K	Pressure range, bar	Number of points	Ref.	EoS	Mixing rule: vdW1	
					k_{ij}	AARD
308.2	80.4-203.5	45	21	PR	0.17473	15.393
				SRK	0.15177	14.203
308.2	83.6-483.4	7	24	PR	0.14900	14.126
				SRK	0.16027	16.301
318.2	95-254	20	21	PR	0.11393	10.934
				SRK	0.12859	11.304
323.15	104.3-483.4	7	24	PR	0.142989	23.531
				SRK	0.14786	28.384
328.2	105-245	20	21	PR	0.12848	8.282
				SRK	0.15626	7.827
343.1	104.3-483.4	8	24	PR	0.17827	34.283
				SRK	0.19383	37.292
Component: Pyrene						
T / K	Pressure range, bar	Mixing rule: vdW2			Mixing rule: CVD	
		k_{ij}	l_{ij}	AARD	M_{ij}	AARD
308.2	80.4-203.5	0.19193	0.17736	13.102	0.93736	18.403
		0.18436	0.16382	13.872	0.89273	16.302
308.2	83.6-483.4	0.13469	0.16226	12.638	0.91920	18.102
		0.14892	0.29847	15.392	0.93747	20.102
318.2	95-254	0.18943	0.09848	9.029	0.96282	11.103
		0.15839	0.11483	10.903	0.92726	13.203
323.1	104.3-483.4	0.12978	0.15030	12.550	0.90283	28.039
		0.13718	0.49999	18.922	0.89293	36.304
328.2	105-245	0.17837	0.13727	7.928	0.96635	11.048
		0.18173	0.17165	6.239	0.92374	9.093
343.15	104.3-483.4	0.26473	0.20198	26.303	0.89276	35.34
		0.21283	0.26438	30.202	0.80837	40.303

Component: Stearic acid						
T / K	Pressure range, bar	Number of points	Ref.	EoS	Mixing rule: vdW1	
					k_{ij}	AARD
318.1	145.4-361.5	6	16	PR	0.05372	17.309
				SRK	0.06838	16.093
328.1	154.8-467.5	6	16	PR	0.078283	25.320
				SRK	0.04829	32.292
338.1	161.5-463.8	5	16	PR	0.00017	41.039
				SRK	0.01736	40.293
Component: Stearic acid						
T / K	Pressure range, bar	Mixing rule: vdW2			Mixing rule: CVD	
		k_{ij}	l_{ij}	AARD	M_{ij}	AARD
318.1	145.4-361.5	0.01837	0.01288	10.010	0.89264	20.293
		0.02913	0.00182	11.202	0.82615	21.303
328.1	154.8-467.5	0.09837	0.16373	16.028	0.79374	34.204
		0.11433	0.26736	17.439	0.79832	40.203
338.1	161.5-463.8	0.11284	0.21938	20.202	0.81763	50.393
		0.02737	0.32278	21.239	0.89274	49.202