Property Data
(T in K, P in Pa):

$Tc := 561.75$ $\quad Pc := 48.76 \cdot 10^5$ $\quad R := 8.314$

Non Cubic EOS Constants:

$T := 370$

$\varepsilon c := 2.75965 R \cdot Tc$ $\quad bc := 0.20293 R \cdot \frac{Tc}{Pc}$ $\quad k := \begin{pmatrix} -1.04387 \\ 4.53723 \end{pmatrix}$

Adjustable Parameters:

$\alpha 0 := 0.2441$ $\quad \alpha 1 := -0.9541$ $\quad \alpha 2 := 0.9777$ $\quad \beta := 0.3127$ $\quad MBenzene := 78.1118$

$$b(T, \beta, bc) := bc \cdot \left(\frac{1 - \frac{1}{3} \cdot \exp\left(\frac{-\beta \cdot Tc}{T}\right)}{1 - \frac{1}{3} \cdot \exp(-\beta)} \right)$$

Covolume Soft-core Parameter

$$Zrep(\eta) := \frac{4 \cdot \eta - 2 \cdot \eta^2}{(1 - \eta)^3}$$

Compressibillity Factor

$$Arep(\eta) := \frac{4 \cdot \eta - 3\eta^2}{(1 - \eta)^2}$$

Residual Helmholtz Energy

$T := 370$

$$\alpha(T, \alpha 0, \alpha 1, \alpha 2) := \alpha 0 + \alpha 1 \cdot \frac{T}{Tc} + \alpha 2 \cdot \left(\frac{T}{Tc}\right)^2$$

Dispersion Energy Parameter

$$\varepsilon(T, \varepsilon c, \alpha 0, \alpha 1, \alpha 2) := \varepsilon c \cdot \frac{1 + \frac{\alpha(T, \alpha 0, \alpha 1, \alpha 2) \cdot Tc}{T}}{1 + \alpha(T, \alpha 0, \alpha 1, \alpha 2)}$$

$$Zdisp(\eta, \varepsilon c, T, \alpha 0, \alpha 1, \alpha 2) := -\left[\frac{4 \varepsilon(T, \varepsilon c, \alpha 0, \alpha 1, \alpha 2)}{R \cdot T} \cdot \eta \cdot \left(1 + k_0 \cdot \eta + k_1 \cdot \eta^2\right)\right]$$

Compressibillity Factor

$$Adisp(\eta, \varepsilon c, T, \alpha 0, \alpha 1, \alpha 2) := -\left[\frac{4\cdot\varepsilon(T, \varepsilon c, \alpha 0, \alpha 1, \alpha 2)}{R\cdot T}\cdot\eta\cdot\left(1 + \frac{1}{2}\cdot k_0\cdot\eta + \frac{1}{3}\cdot k_1\cdot\eta^2\right)\right]$$

Residual Helmholtz Energy

Two Equal Sites

Association Energy Parameter

$Vaa := 0.0$ $\varepsilon aa := 0.0$

$$H(T, Vaa, \varepsilon aa) := Vaa\cdot\left(\exp\left(\frac{\varepsilon aa\cdot Tc}{T}\right) - 1\right)$$

$$Zrep(\eta) := \frac{4\cdot\eta - 2\cdot\eta^2}{(1-\eta)^3}$$

$$Xa(\eta, T, Vaa, \varepsilon aa) := \frac{2}{\left(1 + \sqrt{1 + Zrep(\eta)\cdot H(T, Vaa, \varepsilon aa)}\right)}$$

$$Zass(\eta, T, Vaa, \varepsilon aa) := -0.5\cdot H(T, Vaa, \varepsilon aa)\cdot\frac{2\cdot\eta + 2\cdot\eta^2 - \eta^3}{(1-\eta)^4}\cdot Xa(\eta, T, Vaa, \varepsilon aa)^2$$

$$Aass(\eta, T, Vaa, \varepsilon aa) := (2\cdot\ln(Xa(\eta, T, Vaa, \varepsilon aa)) - Xa(\eta, T, Vaa, \varepsilon aa) + 1)$$

Solution iterating on Reduced Densities

$$Z(\eta, \varepsilon c, T, \alpha 0, \alpha 1, \alpha 2, Vaa, \varepsilon aa) := 1 + Zrep(\eta) + Zdisp(\eta, \varepsilon c, T, \alpha 0, \alpha 1, \alpha 2) + Zass(\eta, T, Vaa, \varepsilon aa)$$

$$A(\eta, T, \varepsilon c, \alpha 0, \alpha 1, \alpha 2, Vaa, \varepsilon aa, \beta, bc) := R\cdot T\cdot(Arep(\eta) + Adisp(\eta, \varepsilon c, T, \alpha 0, \alpha 1, \alpha 2) + Aass(\eta, T, Vaa, \varepsilon aa)) + R$$

$$P(\eta, \varepsilon c, T, \alpha 0, \alpha 1, \alpha 2, Vaa, \varepsilon aa, \beta, bc) := Z(\eta, \varepsilon c, T, \alpha 0, \alpha 1, \alpha 2, Vaa, \varepsilon aa)\cdot R\cdot T\cdot 4\cdot\frac{\eta}{b(T, \beta, bc)}$$

Experimental Data

Benzene :=

278.70	0.047988	893.64
283.70	0.062570	888.58
288.70	0.080685	883.44
293.70	0.10297	878.26
298.70	0.13014	873.02
303.70	0.16297	867.74
308.70	0.20233	862.42
313.70	0.24913	857.06
318.70	0.30440	851.66
323.70	0.36921	846.24
328.70	0.44472	840.78
333.70	0.53215	835.28
338.70	0.63279	829.76
343.70	0.74800	824.20
348.70	0.87920	818.60
353.70	1.0279	812.97
358.70	1.1956	807.30
363.70	1.3839	801.59
368.70	1.5945	795.84
373.70	1.8290	790.04
378.70	2.0893	784.18
383.70	2.3770	778.28
388.70	2.6941	772.32
393.70	3.0423	766.29
398.70	3.4236	760.20
403.70	3.8400	754.04
408.70	4.2934	747.79
413.70	4.7858	741.47
418.70	5.3192	735.06
423.70	5.8958	728.54
428.70	6.5176	721.93
433.70	7.1868	715.20
438.70	7.9055	708.35
443.70	8.6760	701.37
448.70	9.5005	694.25
453.70	10.381	686.97
458.70	11.321	679.53
463.70	12.321	671.90

463.70	12.321	671.90
468.70	13.385	664.08
473.70	14.515	656.04
478.70	15.714	647.76
483.70	16.983	639.22
488.70	18.327	630.38
493.70	19.747	621.22
498.70	21.247	611.70
503.70	22.830	601.76
508.70	24.500	591.34
513.70	26.258	580.38
518.70	28.111	568.78
523.70	30.061	556.42
528.70	32.113	543.12
533.70	34.273	528.65
538.70	36.547	512.64
543.70	38.941	494.52
548.70	41.466	473.19
553.70	44.135	446.22
558.70	46.973	404.91

Fitting Procedure

Guess Values

$\varepsilon c := 2.75965 \cdot R \cdot Tc$ $\quad bc := 0.20293 \cdot R \cdot \frac{Tc}{Pc}$

Input Parameters

$\alpha 0 := 0.2441 \quad \alpha 1 := -0.9541 \quad \alpha 2 := 0.9777 \quad \beta := 0.3127$

Adjustable Parameters

$Vaa := 0.0 \quad \varepsilon aa := 0.0 \quad bc = 0.000194372876$

Semiadjustable Parameters

$\eta c := 0.15$

$\eta := \eta c \quad T := Tc$

$TOL := 0.01 \quad CTOL := 0.01$

Given

$$bc = \frac{Z(\eta, \varepsilon c, T, \alpha 0, \alpha 1, \alpha 2, Vaa, \varepsilon aa) \cdot \eta \cdot R \cdot Tc \cdot 4}{Pc}$$

$\varepsilon c = 12888.640383675$

$bc = 0.000194372876$

$$\frac{d}{d\eta}(P(\eta,\varepsilon c,T,\alpha 0,\alpha 1,\alpha 2,Vaa,\varepsilon aa,\beta,bc)) = 0$$

$$\frac{d^2}{d\eta^2}P(\eta,\varepsilon c,T,\alpha 0,\alpha 1,\alpha 2,Vaa,\varepsilon aa,\beta,bc) = 0$$

$Fcrit := Find(\eta,\varepsilon c,bc)$

Critical Parameters (solving system of two non linear equations)

$\eta c := Fcrit_0$ $\varepsilon c := Fcrit_1$ $bc := Fcrit_2$ $Fcrit_1 = 12888.677816627092$

$$bc := 4\cdot\frac{Z(\eta,\varepsilon c,T,\alpha 0,\alpha 1,\alpha 2,Vaa,\varepsilon aa)\cdot\eta c\cdot R\cdot Tc}{Pc}$$

$Fcrit_0 = 0.158301001011$

$\eta v := 0.0001$ $\eta l := 0.6$ $bc = 0.00020509446$

$T := Benzene_{50,0}$ $T := 298.15$

Given

$$A(\eta l,T,\varepsilon c,\alpha 0,\alpha 1,\alpha 2,Vaa,\varepsilon aa,\beta,bc) + P(\eta l,\varepsilon c,T,\alpha 0,\alpha 1,\alpha 2,Vaa,\varepsilon aa,\beta,bc)\cdot\frac{b(T,\beta,bc)}{4\cdot\eta l} = A$$

$$P(\eta v,\varepsilon c,T,\alpha 0,\alpha 1,\alpha 2,Vaa,\varepsilon aa,\beta,bc) = P(\eta l,\varepsilon c,T,\alpha 0,\alpha 1,\alpha 2,Vaa,\varepsilon aa,\beta,bc)$$

$Sol(T,\alpha 0,\alpha 1,\alpha 2,Vaa,\varepsilon aa,\beta) := Find(\eta v,\eta l)$

$Sol(T,\alpha 0,\alpha 1,\alpha 2,Vaa,\varepsilon aa,\beta)_0 = 0.000147138045$

$Sol(T,\alpha 0,\alpha 1,\alpha 2,Vaa,\varepsilon aa,\beta)_1 = 0.58223488631$

$P\left(Sol(T,\alpha 0,\alpha 1,\alpha 2,Vaa,\varepsilon aa,\beta)_0,\varepsilon c,T,\alpha 0,\alpha 1,\alpha 2,Vaa,\varepsilon aa,\beta,bc\right) = 6582.863196660976$

$Z(\eta v,\varepsilon c,T,\alpha 0,\alpha 1,\alpha 2,Vaa,\varepsilon aa) = 0.998296687966$ $Z(\eta l,\varepsilon c,T,\alpha 0,\alpha 1,\alpha 2,Vaa,\varepsilon a$

$N := 50$

$P(\eta v,\varepsilon c,T,\alpha 0,\alpha 1,\alpha 2,Vaa,\varepsilon aa,\beta,bc) = 4477.537026975479$

$P(\eta l,\varepsilon c,T,\alpha 0,\alpha 1,\alpha 2,Vaa,\varepsilon aa,\beta,bc) = 51589822.333832487$

$$\text{Texp} := \left| \begin{array}{l} \text{for } i \in 0..N-1 \\ \quad \text{Texp}_i \leftarrow \text{Benzene}_{i,0} \\ \text{Texp} \end{array} \right.$$

$$\text{Pexp} := \left| \begin{array}{l} \text{for } i \in 0..N-1 \\ \quad \text{Pexp}_i \leftarrow \text{Benzene}_{i,1} \cdot 10^5 \\ \text{Pexp} \end{array} \right.$$

$$\rho\text{lexp} := \left| \begin{array}{l} \text{for } i \in 0..N-1 \\ \quad \rho\text{lexp}_i \leftarrow \dfrac{\text{Benzene}_{i,}}{\text{MBenzen}} \\ \rho\text{lexp} \end{array} \right.$$

$$\begin{pmatrix} \alpha 0 \\ \alpha 1 \\ \alpha 2 \\ \beta \end{pmatrix} = \begin{pmatrix} 0.2441 \\ -0.9541 \\ 0.9777 \\ 0.3127 \end{pmatrix}$$

$$\text{TOL} := 10^{-12}$$

$$\text{Benzene}_{1,1} = 0$$

$$\text{MBenzene} = 78.1118$$

$$\text{CTOL} = 0.01$$

Given

Calculate

$$\sum_{i=0}^{N-1} \left(500 \cdot \frac{P\left(\text{Sol}\left(\text{Texp}_i, \alpha 0, \alpha 1, \alpha 2, \text{Vaa}, \varepsilon\text{aa}, \beta\right)_0, \varepsilon c, \text{Texp}_i, \alpha 0, \alpha 1, \alpha 2, \text{Vaa}, \varepsilon\text{aa}, \beta, \text{bc}\right) - \text{Pexp}_i}{\text{Pexp}_i} \right) :$$

$$\sum_{i=0}^{N-1} \left[100 \cdot \left[\frac{\dfrac{4 \cdot \left(\text{Sol}\left(\text{Texp}_i, \alpha 0, \alpha 1, \alpha 2, \text{Vaa}, \varepsilon\text{aa}, \beta\right)_1\right) \cdot 10^{-3}}{b\left(\text{Texp}_i, \beta, \text{bc}\right)} - \rho\text{lexp}_i}{\rho\text{lexp}_i} \right] \right] = 0$$

$$\begin{pmatrix} \alpha 0n \\ \alpha 1n \\ \alpha 2n \\ \beta n \end{pmatrix} := \text{Minerr}(\alpha 0, \alpha 1, \alpha 2, \beta)$$

$$\begin{pmatrix} \alpha 0n \\ \alpha 1n \\ \alpha 2n \\ \beta \end{pmatrix} = \begin{pmatrix} 0.2441 \\ -0.9541 \\ 0.9777 \\ 0.3127 \end{pmatrix}$$

$$ADP := 100 \cdot \frac{\sum_{i=0}^{N-1} \left(\frac{P\left(Sol\left(Texp_i, \alpha 0n, \alpha 1n, \alpha 2n, Vaa, \varepsilon aa, \beta\right)_0, \varepsilon c, Texp_i, \alpha 0n, \alpha 1n, \alpha 2n, Vaa, \varepsilon aa, \beta n, \mathrm{l}\right.}{Pexp_i} \right.}{N}$$

$ADP = -28.546938424616$

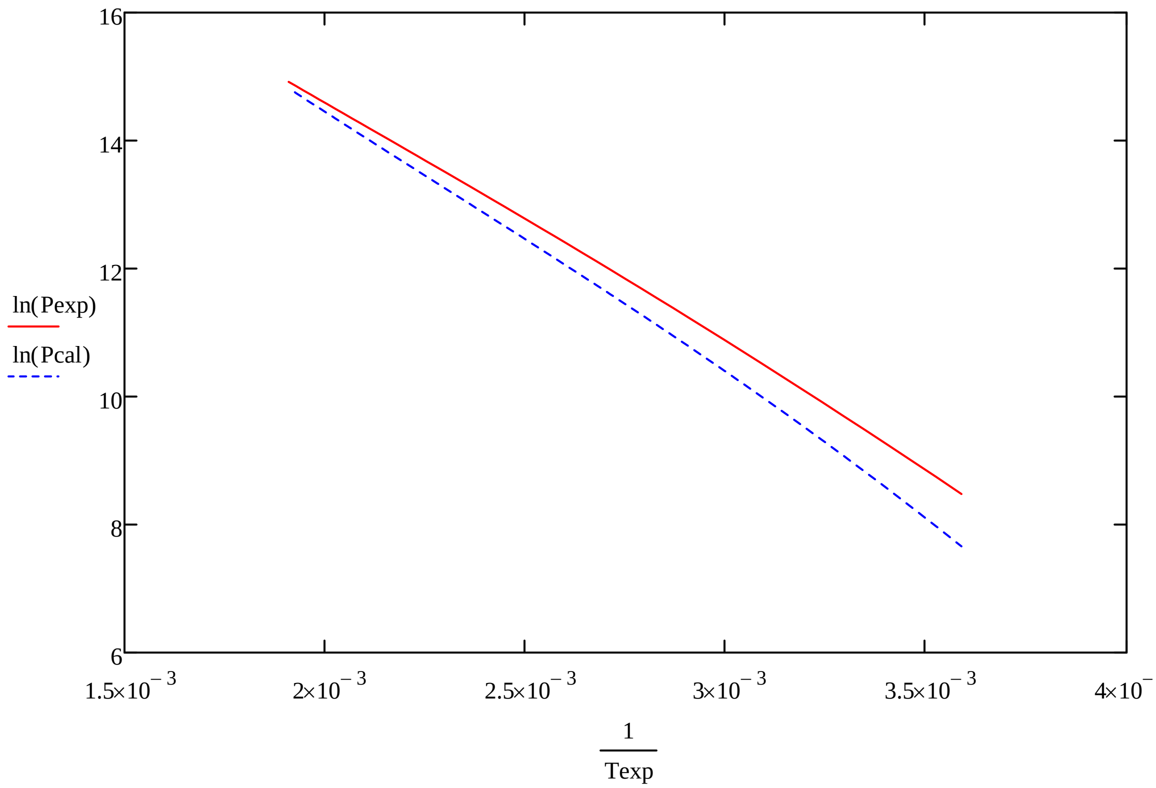
$$ADrho := 100 \cdot \frac{\sum_{i=0}^{N-1} \left[\frac{\frac{4 \cdot \left(Sol\left(Texp_i, \alpha 0, \alpha 1, \alpha 2, Vaa, \varepsilon aa, \beta\right)_1\right) \cdot 10^{-3}}{b\left(Texp_i, \beta, bc\right)} - \rho lexp_i}{\rho lexp_i} \right]}{N}$$

$ADrho = -5.843781093948$

$$Pcal := \left| \begin{array}{l} \text{for } i \in 0 .. N-1 \\ \quad Pcal_i \leftarrow P\left(Sol\left(Texp_i, \alpha 0n, \alpha 1n, \alpha 2n, Vaa, \varepsilon aa, \beta\right)_0, \varepsilon c, Texp_i, \alpha 0n, \alpha 1n, \mathrm{c} \right. \\ Pcal \end{array} \right.$$

$$\rho cal := \left| \begin{array}{l} \text{for } i \in 0 .. N-1 \\ \quad \rho cal_i \leftarrow \frac{4 \cdot \left(Sol\left(Texp_i, \alpha 0, \alpha 1, \alpha 2, Vaa, \varepsilon aa, \beta\right)_1\right) \cdot 10^{-3}}{b\left(Texp_i, \beta, bc\right)} \\ \rho cal \end{array} \right.$$

$$P\left(Sol\left(Texp_i, \alpha 0, \alpha 1, \alpha 2, Vaa, \varepsilon aa, \beta\right)_0, \varepsilon c, Texp_i, \alpha 0, \alpha 1, \alpha 2, Vaa, \varepsilon aa, \beta\right)$$



εc = 12888.677816627092

bc = 0.00020509446

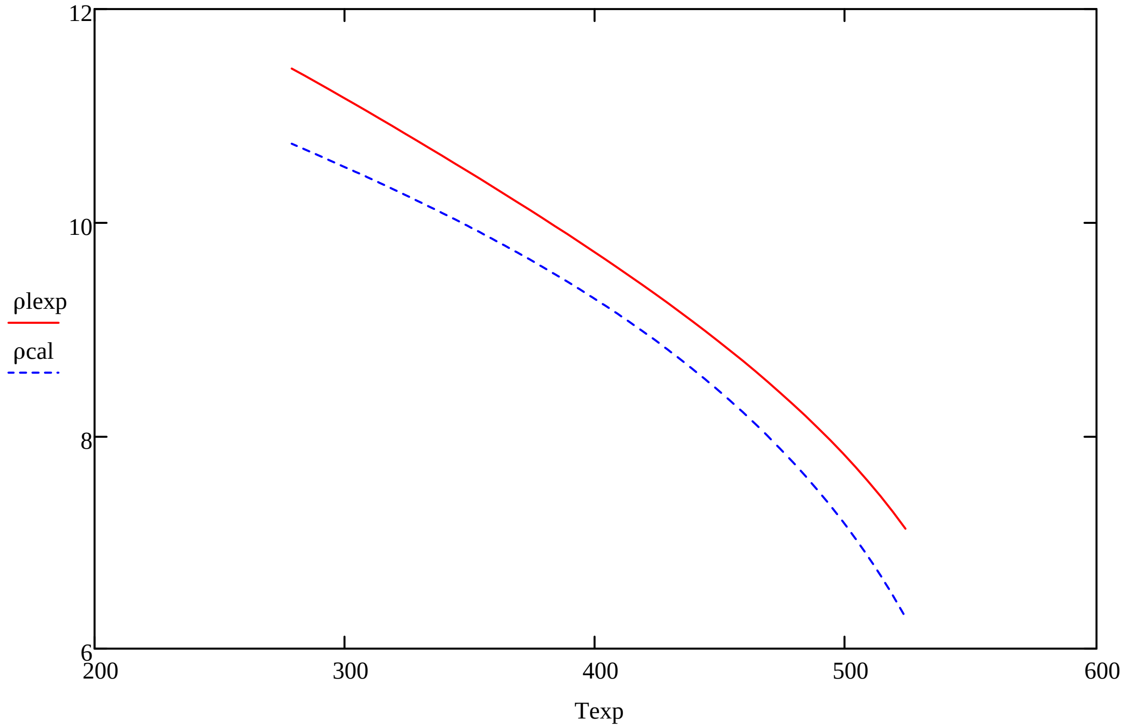
$$\begin{pmatrix} \alpha 0n \\ \alpha 1n \\ \alpha 2n \\ \beta n \\ \varepsilon aa \\ Vaa \end{pmatrix} = \begin{pmatrix} 0.2441 \\ -0.9541 \\ 0.9777 \\ 0.3127 \\ 0 \\ 0 \end{pmatrix}$$

Pcal =

	0
0	2114.555865703804
1	2894.209583936
2	3898.761845712283
3	5175.248519553594
4	6776.703243527607
5	8762.366532499635
6	11197.864134421769
7	14155.35975526746
8	17713.687628397824
9	21958.470403811509
10	26982.22754869983
11	32884.47895800331
12	39771.847843011834
13	47758.166259729966
14	56964.585908412606
15	...

Pexp =

	0
0	4798.8
1	6257
2	8068.500000000001
3	10297
4	13014
5	16297
6	20233
7	24913
8	30440
9	36921
10	44472
11	53215
12	63279
13	74800
14	87920
15	...



ρcal =

	0
0	10.735015123223
1	10.684307676685
2	10.633124130919
3	10.58142940119
4	10.529186617647
5	10.476357116684
6	10.422900422269
7	10.36877421624
8	10.313934296496
9	10.25833452201
10	10.201926743484
11	10.144660718373
12	10.086484008873
13	10.027341861289
14	9.967177064984

ρlexp =

	0
0	11.440524991102
1	11.375746046052
2	11.309942927957
3	11.24362772334
4	11.17654438894
5	11.108948968018
6	11.040841460573
7	10.972221866607
8	10.903090186118
9	10.833702462368
10	10.763802652096
11	10.693390755302
12	10.622722815247
13	10.55154278867
14	10.47985067557

15	...

14	10.47985067557
15	...