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

$Tc := 647.3$ $Pc := 221.2 \cdot 10^5$ $R := 8.314$

$T := 370$

**Water**

**Non Cubic EOS Constants:**

$\varepsilon c := 13639.420560723906$ $bc := 0.000054817616$ $k := \begin{pmatrix} -1.04387 \\ 4.53723 \end{pmatrix}$

**Input Guess Parameters**

**Adjustable Parameters:**

$\alpha 0 := 0.202093990261$ $\alpha 1 := -0.694066100483$ $\alpha 2 := 0.514593582392$ $\beta := 0.304713666986$

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

**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

$Vaa := 0.05$

$\varepsilon aa := 2.0$

**Association Energy Parameter**

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

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

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

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

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

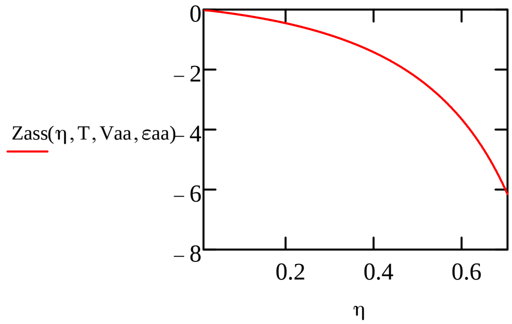
## Solution iterating on Reduced Densities

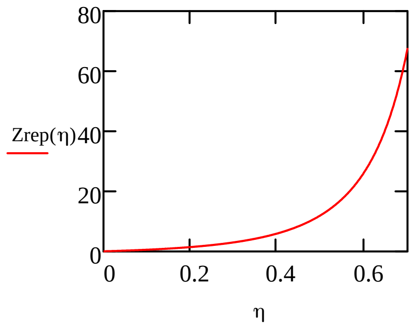
$$Z(\eta, \varepsilon c, T, \alpha 0, \alpha 1, \alpha 2, Vaa, \varepsilon aa) := 1 + Zrep(\eta) + Zdisp(\eta, \varepsilon c, T, \alpha 0, \alpha 1, \alpha 2) + Zass(\eta, T, Vaa, \varepsilon aa)$$

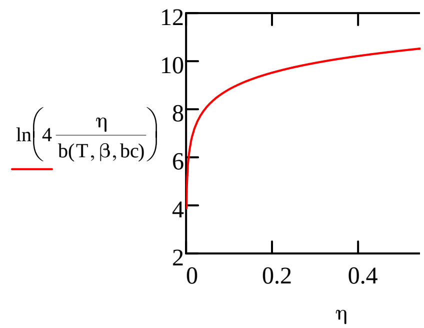
$$A(\eta, T, \alpha 0, \alpha 1, \alpha 2, Vaa, \varepsilon aa, \beta) := R\cdot T\cdot(Arep(\eta) + Adisp(\eta, \varepsilon c, T, \alpha 0, \alpha 1, \alpha 2) + Aass(\eta, T, Vaa, \varepsilon aa)) + R\cdot T\cdot\ln\left(4\frac{\eta}{b(T, \beta, bc)}\right)$$

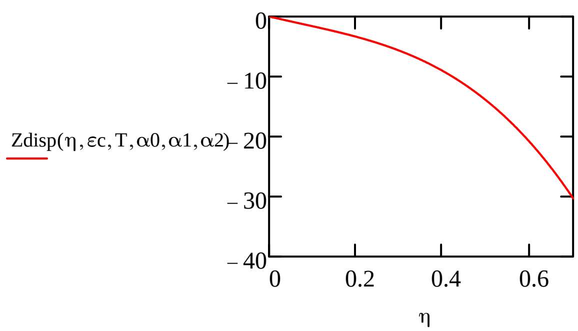
$$P(\eta, \varepsilon c, T, \alpha 0, \alpha 1, \alpha 2, Vaa, \varepsilon aa, \beta, bc) := Z(\eta, \varepsilon c, T, \alpha 0, \alpha 1, \alpha 2, Vaa, \varepsilon aa)\cdot R\cdot T\cdot 4\cdot\frac{\eta}{b(T, \beta, bc)}$$

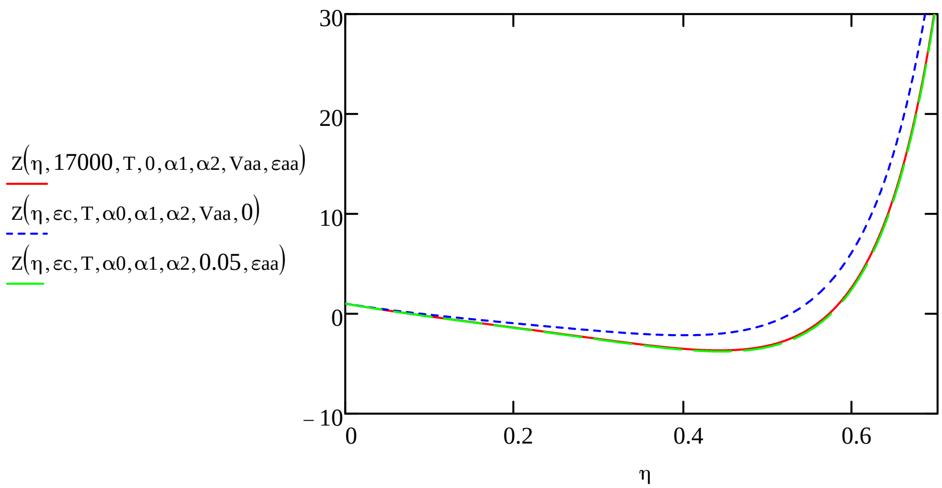
R·T =


0
– 2
Zass(η, T, Vaa, εaa)– 4
– 6
– 8
0.2
0.4
0.6
η


80
60
Zrep(η)40
20
0
0
0.2
0.4
0.6
η


12
10
ln(4 η / b(T, β, bc))
8
6
4
2
0
0.2
0.4
η


0
– 10
Zdisp(η, εc, T, α0, α1, α2)– 20
– 30
– 40
0
0.2
0.4
0.6
η




**Experimental Data**

**T[K] P[MPa] rho[liters/mol]**

Water :=

| | | |
|---|---|---|
| 273.16 | 0.00061165 | 55.497 |
| 278.16 | 0.00087318 | 55.504 |
| 283.16 | 0.0012290 | 55.489 |
| 288.16 | 0.0017069 | 55.456 |
| 293.16 | 0.0023408 | 55.406 |
| 298.16 | 0.0031718 | 55.342 |
| 303.16 | 0.0042494 | 55.264 |
| 308.16 | 0.0056321 | 55.175 |
| 313.16 | 0.0073889 | 55.074 |
| 318.16 | 0.0095999 | 54.963 |
| 323.16 | 0.012358 | 54.842 |
| 328.16 | 0.015770 | 54.712 |
| 333.16 | 0.019956 | 54.573 |
| 338.16 | 0.025053 | 54.427 |
| 343.16 | 0.031214 | 54.272 |
| 348.16 | 0.038612 | 54.110 |
| 353.16 | 0.047434 | 53.941 |
| 358.16 | 0.057890 | 53.765 |
| 363.16 | 0.070208 | 53.582 |
| 368.16 | 0.084640 | 53.392 |
| 373.16 | 0.10145 | 53.196 |
| 378.16 | 0.12094 | 52.994 |
| 383.16 | 0.14343 | 52.785 |
| 388.16 | 0.16924 | 52.571 |
| 393.16 | 0.19874 | 52.350 |
| 398.16 | 0.23231 | 52.123 |
| 403.16 | 0.27036 | 51.891 |
| 408.16 | 0.31332 | 51.652 |
| 413.16 | 0.36164 | 51.408 |
| 418.16 | 0.41580 | 51.157 |
| 423.16 | 0.47629 | 50.901 |
| 428.16 | 0.54364 | 50.639 |
| 433.16 | 0.61839 | 50.371 |
| 438.16 | 0.70111 | 50.096 |
| 443.16 | 0.79238 | 49.816 |
| 448.16 | 0.89281 | 49.529 |
| 453.16 | 1.0030 | 49.235 |
| 458.16 | 1.1237 | 48.936 |
| 463.16 | 1.2555 | 48.629 |
| 468.16 | 1.3991 | 48.316 |
| 473.16 | 1.5553 | 47.995 |
| 478.16 | 1.7246 | 47.668 |
| 483.16 | 1.9081 | 47.332 |
| 488.16 | 2.1063 | 46.989 |
| 493.16 | 2.3200 | 46.639 |
| 498.16 | 2.5502 | 46.279 |

| | | |
|---|---|---|
| 503.16 | 2.7976 | 45.911 |
| 508.16 | 3.0631 | 45.534 |
| 513.16 | 3.3475 | 45.148 |
| 518.16 | 3.6518 | 44.751 |
| 523.16 | 3.9768 | 44.345 |
| 528.16 | 4.3236 | 43.927 |
| 533.16 | 4.6930 | 43.497 |
| 538.16 | 5.0861 | 43.055 |
| 543.16 | 5.5038 | 42.600 |
| 548.16 | 5.9473 | 42.130 |
| 553.16 | 6.4176 | 41.646 |
| 558.16 | 6.9157 | 41.145 |
| 563.16 | 7.4429 | 40.626 |
| 568.16 | 8.0003 | 40.088 |
| 573.16 | 8.5891 | 39.528 |
| 578.16 | 9.2107 | 38.946 |
| 583.16 | 9.8664 | 38.337 |
| 588.16 | 10.558 | 37.699 |
| 593.16 | 11.286 | 37.028 |
| 598.16 | 12.053 | 36.319 |
| 603.16 | 12.860 | 35.567 |
| 608.16 | 13.709 | 34.763 |
| 613.16 | 14.603 | 33.895 |
| 618.16 | 15.542 | 32.949 |
| 623.16 | 16.531 | 31.899 |
| 628.16 | 17.572 | 30.701 |
| 633.16 | 18.668 | 29.283 |
| 638.16 | 19.824 | 27.514 |
| 643.16 | 21.046 | 25.052 |
| "" | 0 | 0 |

$N := 40$

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

$$Pexp := \left| \begin{array}{l} \text{for } i \in 0..N-1 \\ \quad Pexp_i \leftarrow Water_{i,1} \cdot 10^6 \\ Pexp \end{array} \right.$$

$$\rho lexp := \left| \begin{array}{l} \text{for } i \in 0..N-1 \\ \quad \rho lexp_i \leftarrow Water_{i,2} \\ \rho lexp \end{array} \right.$$

$$\eta vexp := \left| \begin{array}{l} \text{for } i \in 0..N-1 \\ \quad \eta vexp_i \leftarrow \dfrac{Pexp_i \cdot bc}{R \cdot Texp_i \cdot 4} \\ \eta vexp \end{array} \right.$$

$$\eta lexp := \left| \begin{array}{l} \text{for } i \in 0..N-1 \\ \quad \eta lexp_i \leftarrow \dfrac{\rho lexp_i \cdot bc \cdot 10^3}{4} \\ \eta lexp \end{array} \right.$$

**Fitting Procedure**

$\varepsilon c = 13639.420560723906$ $\quad bc = 0.000054817616$

**Critical Parameters**

$\alpha 0 := 0.0$ $\quad \alpha 1 := 0.0$ $\quad \alpha 2 := 0.0$ $\quad \beta := 0.3048233$

**Temperature Dependence Parameters**

$Vaa := 0.05$ $\quad \varepsilon aa := 2.0$

**Associating Parameters**

Note: Numerical Problem on Van der Waals inflection point conditions here below increasing the association contribution

$\eta c := 0.2$

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

**Van der Waals inflection point conditions**

Given

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

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

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

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

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

$Fcrit_0 = 0.176282784792$ $\quad Fcrit_1 = 13639.420560723947$ $\quad bc = 0.000054817616$

**Tolerances**

$TOL := 10^{-5}$ $\quad CTOL := 10^{-5}$

$\eta v := \eta vexp_0$ $\quad \eta l := \eta lexp_0$ $\quad P1 := Pexp_0$

**Initial Values**

$T := Water_{0,0}$ $\varepsilon aa := 2.0$ $Vaa := 0.05$ **Guess values associating**

**Vapor - Liquid Equilibrium**

Given

$$P(\eta v, \varepsilon c, T, \alpha 0, \alpha 1, \alpha 2, Vaa, \varepsilon aa, \beta, bc) = P1$$

$$P(\eta l, \varepsilon c, T, \alpha 0, \alpha 1, \alpha 2, Vaa, \varepsilon aa, \beta, bc) = P1$$

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

$$Sol(T, \alpha 0, \alpha 1, \alpha 2, Vaa, \varepsilon aa, \beta, \eta v, \eta l, P1) := Find(\eta v, \eta l, P1)$$

$$Sol(T, \alpha 0, \alpha 1, \alpha 2, Vaa, \varepsilon aa, \beta, \eta v, \eta l, P1)_0 = 0.000000699696$$

$$Sol(T, \alpha 0, \alpha 1, \alpha 2, Vaa, \varepsilon aa, \beta, \eta v, \eta l, P1)_1 = 0.642404201749$$

$$P\left(Sol(T, \alpha 0, \alpha 1, \alpha 2, Vaa, \varepsilon aa, \beta, \eta v, \eta l, P1)_0, \varepsilon c, T, \alpha 0, \alpha 1, \alpha 2, Vaa, \varepsilon aa, \beta, bc\right) = 104.345384523618$$

$N := 40$

```
Texp := | for i ∈ 0 .. N − 1
        |   Texp_i ← Water_{i,0}
        | Texp

Pexp := | for i ∈ 0 .. N − 1
        |   Pexp_i ← Water_{i,1} · 10^6
        | Pexp

ρlexp := | for i ∈ 0 .. N − 1
         |   ρlexp_i ← Water_{i,2}
         | ρlexp

errors := | for i ∈ 0 .. N − 1
          |   errors_i ← i  on error  0·Sol(Water_{i,0}, α0, α1, α2, Vaa, εaa, β, ηvexp_i, ηlexp_i, Pexp_i)
          | errors
```

errors = 0

$$\begin{pmatrix} \alpha 0 \\ \alpha 1 \\ \alpha 2 \\ \beta \\ \varepsilon aa \\ Vaa \end{pmatrix} := \begin{pmatrix} -0.00542251853 \\ -0.010245365223 \\ -0.019077875069 \\ -0.03325218483 \\ 1.954781421924 \\ 0.045828967104 \end{pmatrix}$$

**Objective Function ( Optimization Algorithm )**

Given

$$\sum_{i=0}^{N-1}\left(500\cdot\frac{P\left(Sol\left(Texp_i,\alpha 0,\alpha 1,\alpha 2,Vaa,\varepsilon aa,\beta,\eta vexp_i,\eta lexp_i,Pexp_i\right)_0,\varepsilon c,Texp_i,\alpha 0,\alpha 1,\alpha 2,Vaa,\varepsilon aa,\beta,bc\right)-Pexp_i}{Pexp_i}\right.$$

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

$$\begin{pmatrix}\alpha 0n\\ \alpha 1n\\ \alpha 2n\\ \beta n\\ \varepsilon aan\\ Vaan\end{pmatrix}:=Minerr(\alpha 0,\alpha 1,\alpha 2,\beta,\varepsilon aa,Vaa)$$

$ERR = 921.37922782537$

$$\begin{pmatrix}\alpha 0n\\ \alpha 1n\\ \alpha 2n\\ \beta n\\ \varepsilon aan\\ Vaan\end{pmatrix}=\begin{pmatrix}-0.002592462683\\ -0.010245365223\\ -0.026890375069\\ -0.03325218483\\ 1.754781421924\\ 0.045366598432\end{pmatrix}$$

$$ADP:=100\cdot\frac{\sum_{i=0}^{N-1}\left(\frac{P\left(Sol\left(Texp_i,\alpha 0n,\alpha 1n,\alpha 2n,Vaan,\varepsilon aan,\beta,\eta vexp_i,\eta lexp_i,Pexp_i\right)_0,\varepsilon c,Texp_i,\alpha 0n,\alpha 1n,\alpha 2n,Vaan,\varepsilon aan,\beta n,bc\right)-Pexp_i}{Pexp_i}\right)}{N}$$

$ADP = -2.17925082414$

$$100\cdot\left[\sum_{i=0}^{N-1}\left(\frac{P\left(Sol\left(Texp_i,\alpha 0n,\alpha 1n,\alpha 2n,Vaan,\varepsilon aan,\beta,\eta vexp_i,\eta lexp_i,Pexp_i\right)_0,\varepsilon c,Texp_i,\alpha 0n,\alpha 1n,\alpha 2n,Vaan,\varepsilon aan,\beta n,bc\right)-Pexp_i}{Pexp_i}\right)\right]=-87.1$$

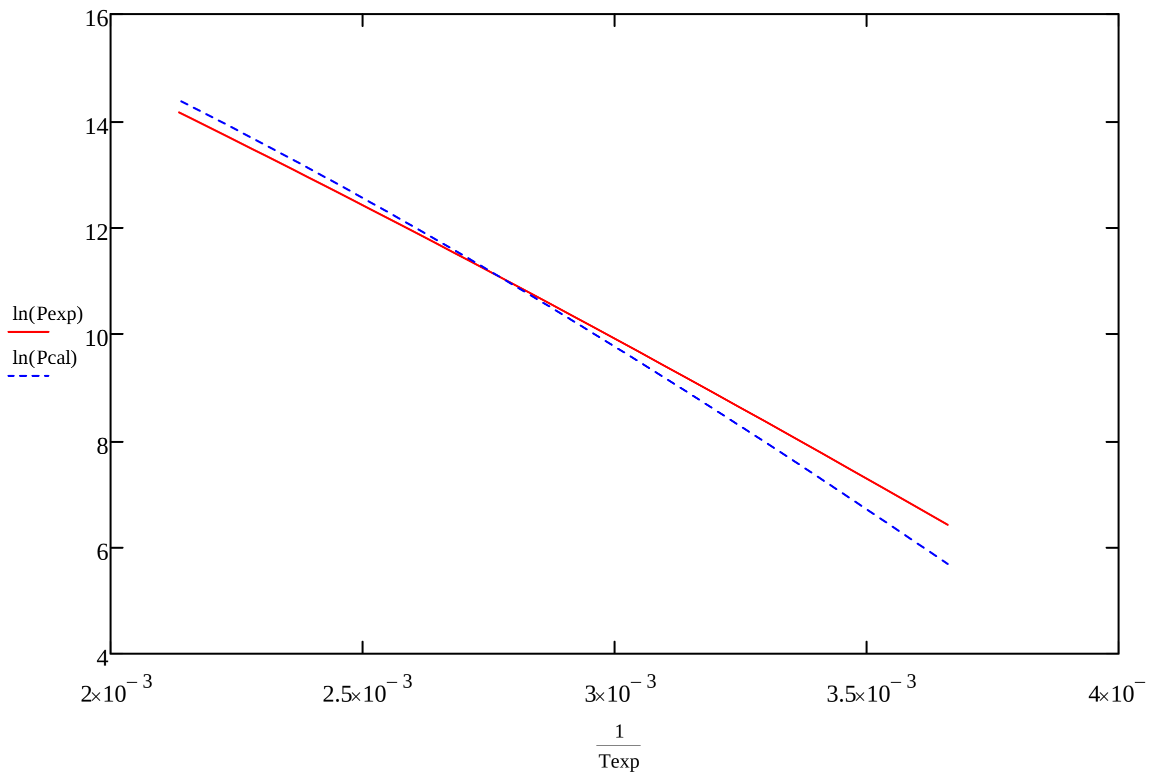
$$ADrho := 100 \cdot \frac{\sum_{i=0}^{N-1} \left[ \frac{\frac{4 \cdot \left( Sol\left(Texp_i, \alpha0n, \alpha1n, \alpha2n, Vaa, \varepsilon aa, \beta n, \eta vexp_i, \eta lexp_i, Pexp_i\right)_1 \right) \cdot 10^{-3}}{b\left(Texp_i, \beta n, bc\right)} - \rho lexp_i}{\rho lexp_i} \right]}{N}$$

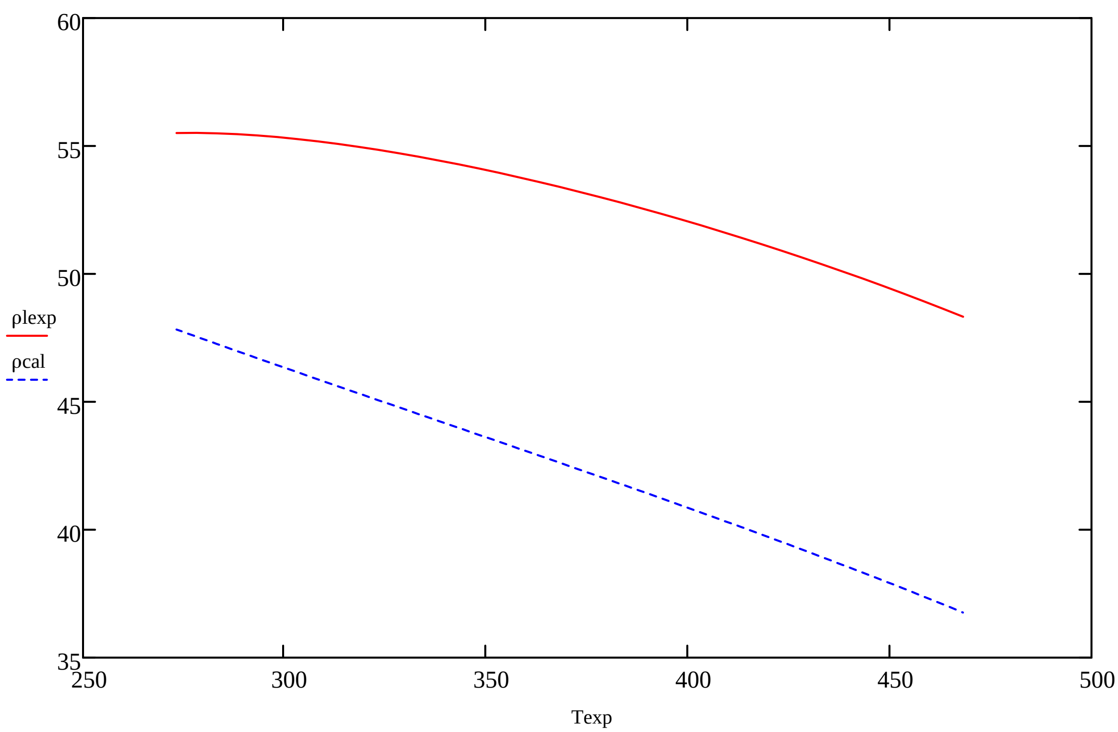
$$ADrho = -19.841081781313$$

$$500 \cdot \left[ \sum_{i=0}^{N-1} \left[ \frac{\frac{4 \cdot \left( Sol\left(Texp_i, \alpha0n, \alpha1n, \alpha2n, Vaa, \varepsilon aa, \beta n, \eta vexp_i, \eta lexp_i, Pexp_i\right)_1 \right) \cdot 10^{-3}}{b\left(Texp_i, \beta n, bc\right)} - \rho lexp_i}{\rho lexp_i} \right] \right] = -3968.216356262581$$

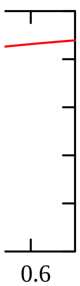
$$Pcal := \begin{array}{|l} \text{for } i \in 0 .. N-1 \\ \quad Pcal_i \leftarrow P\left(Sol\left(Texp_i, \alpha0n, \alpha1n, \alpha2n, Vaan, \varepsilon aan, \beta, \eta vexp_i, \eta lexp_i, Pexp_i\right)_0, \varepsilon c, Texp_i, \alpha0n, \alpha1n, \alpha2n, Vaan, \varepsilon aan, \beta n, bc\right) \\ Pcal \end{array}$$

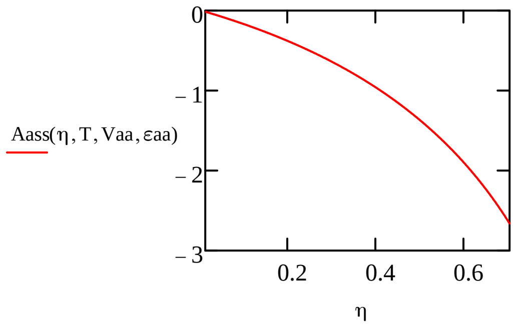
$$\rho cal := \begin{array}{|l} \text{for } i \in 0 .. N-1 \\ \quad \rho cal_i \leftarrow \frac{4 \cdot Sol\left(Texp_i, \alpha0n, \alpha1n, \alpha2n, Vaa, \varepsilon aa, \beta n, \eta vexp_i, \eta lexp_i, Pexp_i\right)_1 \cdot 10^{-3}}{b\left(Texp_i, \beta n, bc\right)} \\ \rho cal \end{array}$$

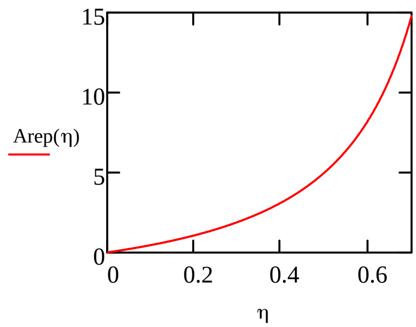

16
14
12
10
8
6
4
ln(Pexp)
ln(Pcal)
2×10−3
2.5×10−3
3×10−3
3.5×10−3
4×10−3
1
Texp

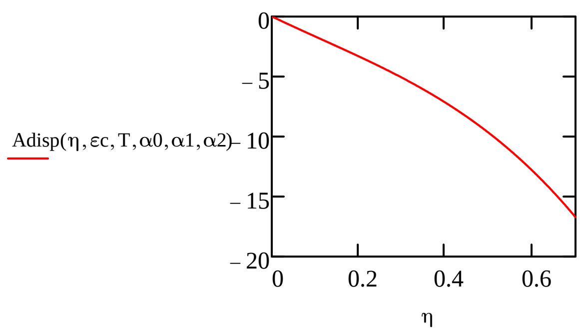

60
55
50
45
40
35
ρlexp
ρcal
250
300
350
400
450
500
Texp

= 3076.18


0.6


0
− 1
− 2
− 3
Aass(η, T, Vaa, εaa)
0.2
0.4
0.6
η


15
10
5
0
Arep(η)
0
0.2
0.4
0.6
η


0
− 5
− 10
− 15
− 20
Adisp(η, εc, T, α0, α1, α2)
0
0.2
0.4
0.6
η

$\varepsilon aa = 2$