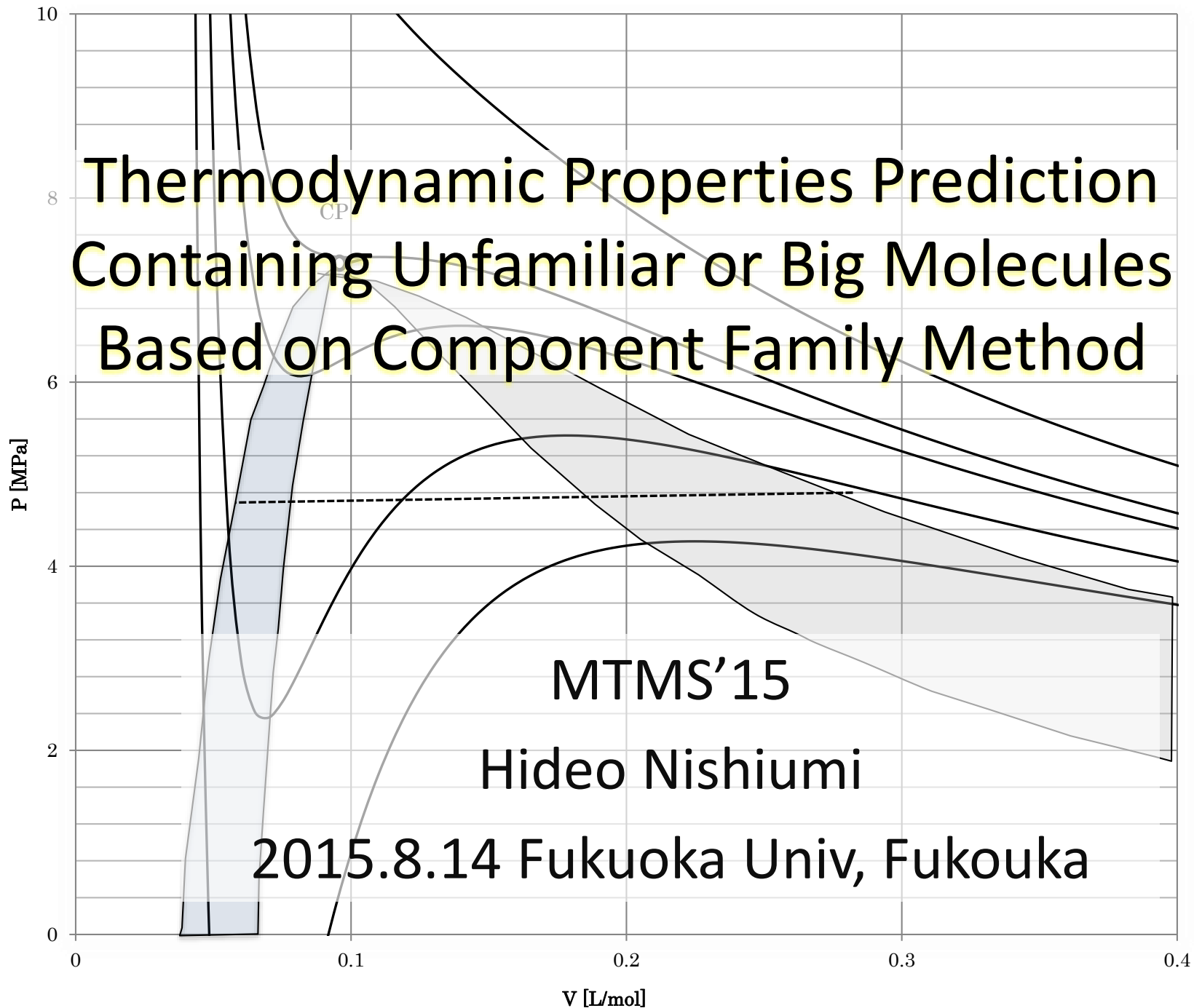
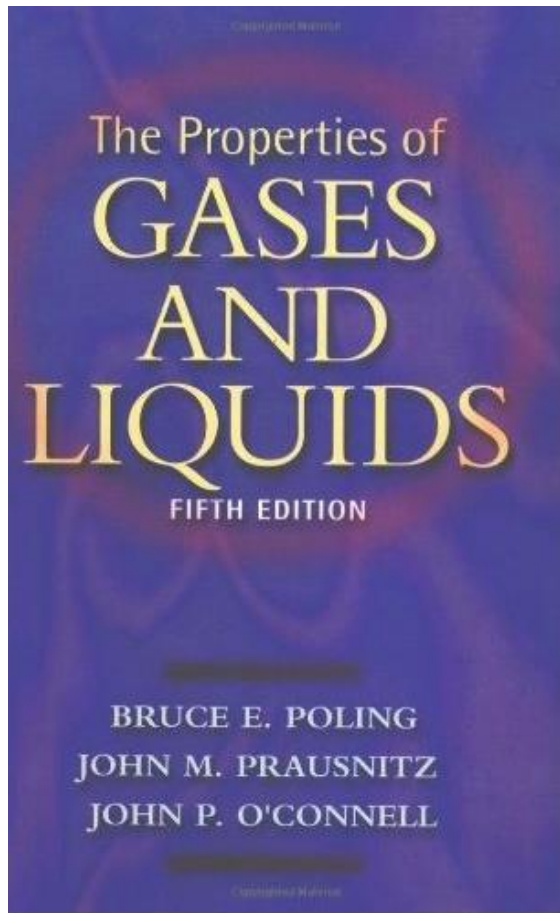


Thermodynamic Properties Prediction Containing Unfamiliar or Big Molecules Based on Component Family Method



Properties Prediction with EoS



(1) Pure properties calculation
Based on Corresponding State
Principle --- Critical Properties -
about 400 Substances are
reported.

To apply to unfamiliar molecules, prediction
of critical properties with group contribution
method is famous

Lydersen (1955)→**Joback (1984)**

Constantinou and Gani (1994)

Wilson and Jasperson (1996)

Marrero and Pardillo (1999)

(2) Mixture properties prediction
Fitting to small amount of VLE data, Binary
interaction parameter, m_{ij} is obtained.

Poling, Prausnitz, O'Connell, Properties of Gases and Liquids
(5th Ed.), McGraw-Hill (2001)

Joback method

TABLE 2-2 Joback Group Contributions for Critical Properties, the Normal Boiling Point, and the Freezing Point

	Δ				
	T_c	P_c	V_c	T_b	T_f
Nonring increments:					
-CH ₃	0.0141	-0.0012	65	23.58	-5.10
>CH ₂	0.0189	0	56	22.88	11.27
>CH-	0.0164	0.0020	41	21.74	12.64
>C<	0.0067	0.0043	27	18.25	46.43
=CH ₂	0.0113	-0.0028	56	18.18	-4.32
=CH-	0.0129	-0.0006	46	24.96	8.73
=C<	0.0117	0.0011	38	24.14	11.14
=C=	0.0026	0.0028	36	26.15	17.78
≡CH	0.0027	-0.0008	46	9.20	-11.18
≡C-	0.0020	0.0016	37	27.38	64.32
Ring increments:					
-CH ₂ -	0.0100	0.0025	48	27.15	7.75
>CH-	0.0122	0.0004	38	21.78	19.88
>C<	0.0042	0.0061	27	21.32	60.15
=CH-	0.0082	0.0011	41	26.73	8.13
=C<	0.0143	0.0008	32	31.01	37.02

$$T_c [\text{K}] = T_b \left[0.584 + 0.965 \sum \Delta_T - \left(\sum \Delta_T \right)^2 \right]^{-1}$$

$$T_b [K] = 198 + \sum \Delta_b$$

$$P_c [\text{MPa}] = 0.1 \times \left(0.113 + 0.0032 n_A - \sum \Delta_P \right)^{-2}$$

$$V_c [\text{cm}^3/\text{mol}] = 17.5 + \sum \Delta_V$$

Critical properties prediction with Joback method

	Av. Dev. [%]
Tc (Tb:experimental)	1.7
Tc (Tb: Group contribut.)	5.9
Pc	6.1
Vc	8.0
For about 400 molecules	

How much deviation will produce when we predict properties using the Joback method ?

Tc prediction with Joback method

- Tetraglyme M.W. 222 Joback method Tc=708 K
- Oleic acid M.W. 283 Joback method: Tc=942 K
- Triolein M.W. 885 Joback method: Tc= 4,019K
- PAG-1 M.W. 1,082 Joback method :Tc= 8,541 K

Failed to predict properties

★ As M.W. increases, big Tc value is obtained –
not for practical use.

First problem with Joback method

$$T_c [\text{K}] = T_b \left[0.584 + 0.965 \sum \Delta_T - \left(\sum \Delta_T \right)^2 \right]^{-1}$$

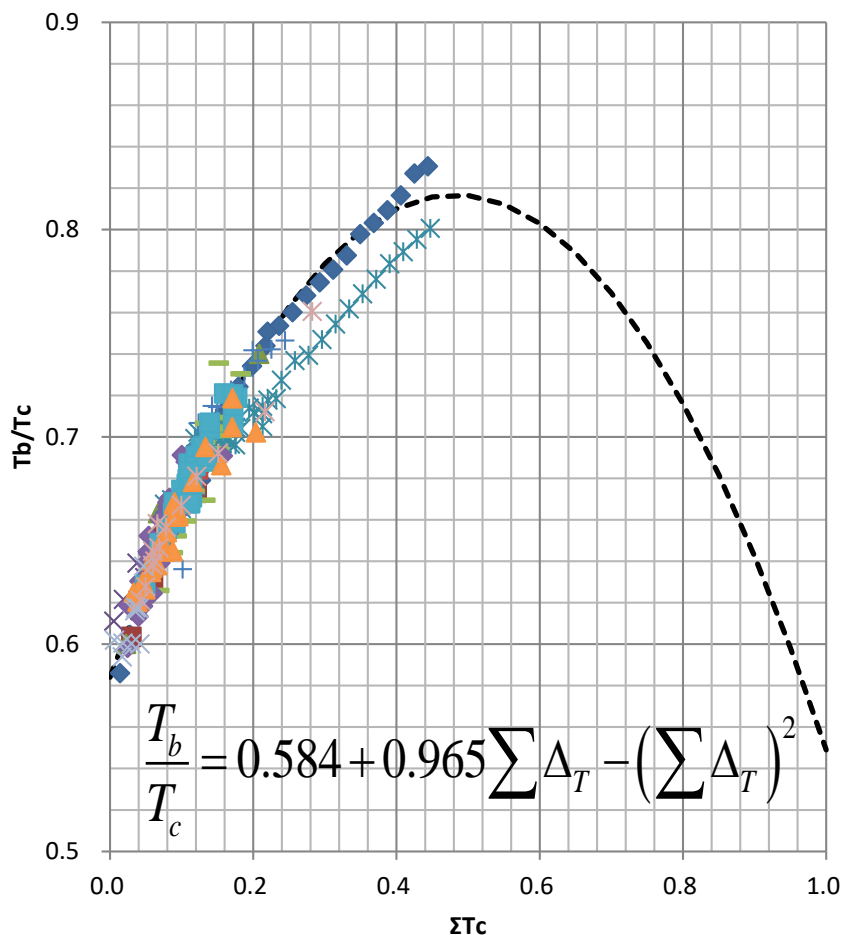
$$T_b [K] = 198 + \sum \Delta_b$$

As T_c is proportional to T_b , too big T_c value is obtained.

Hint to improve prediction of T_c in Joback method

$$\frac{T_b}{T_c} = 0.584 + 0.965 \sum \Delta_T - \left(\sum \Delta_T \right)^2$$

ΣT_c vs. T_b/T_c in Joback method



For about 400 molecules

Except higher alcohols,
Excellent results are
obtained

Observation

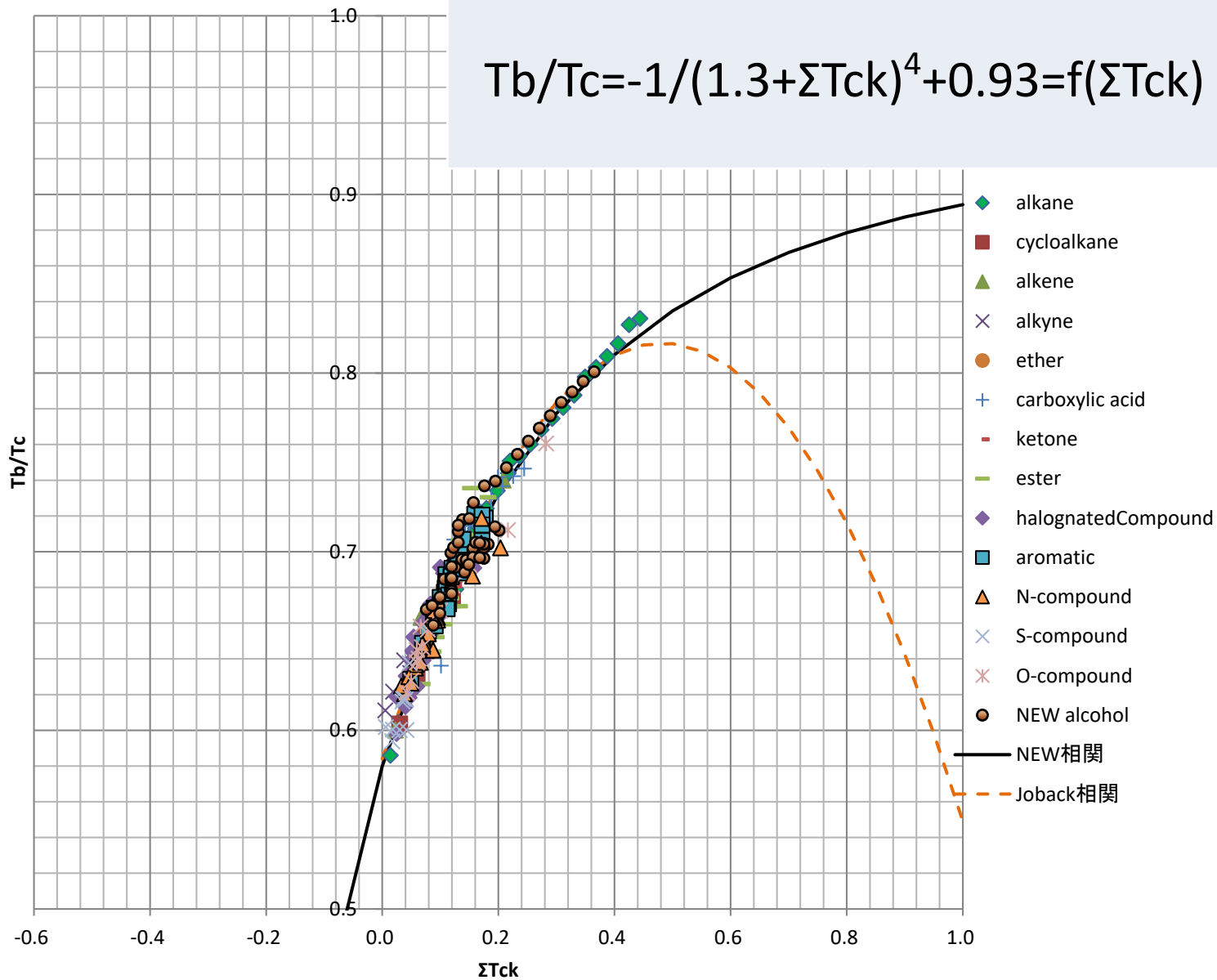
1 : OH contribution for
higher alcohols is
neglected.

2. Maximal of T_b/T_c is
unity at most

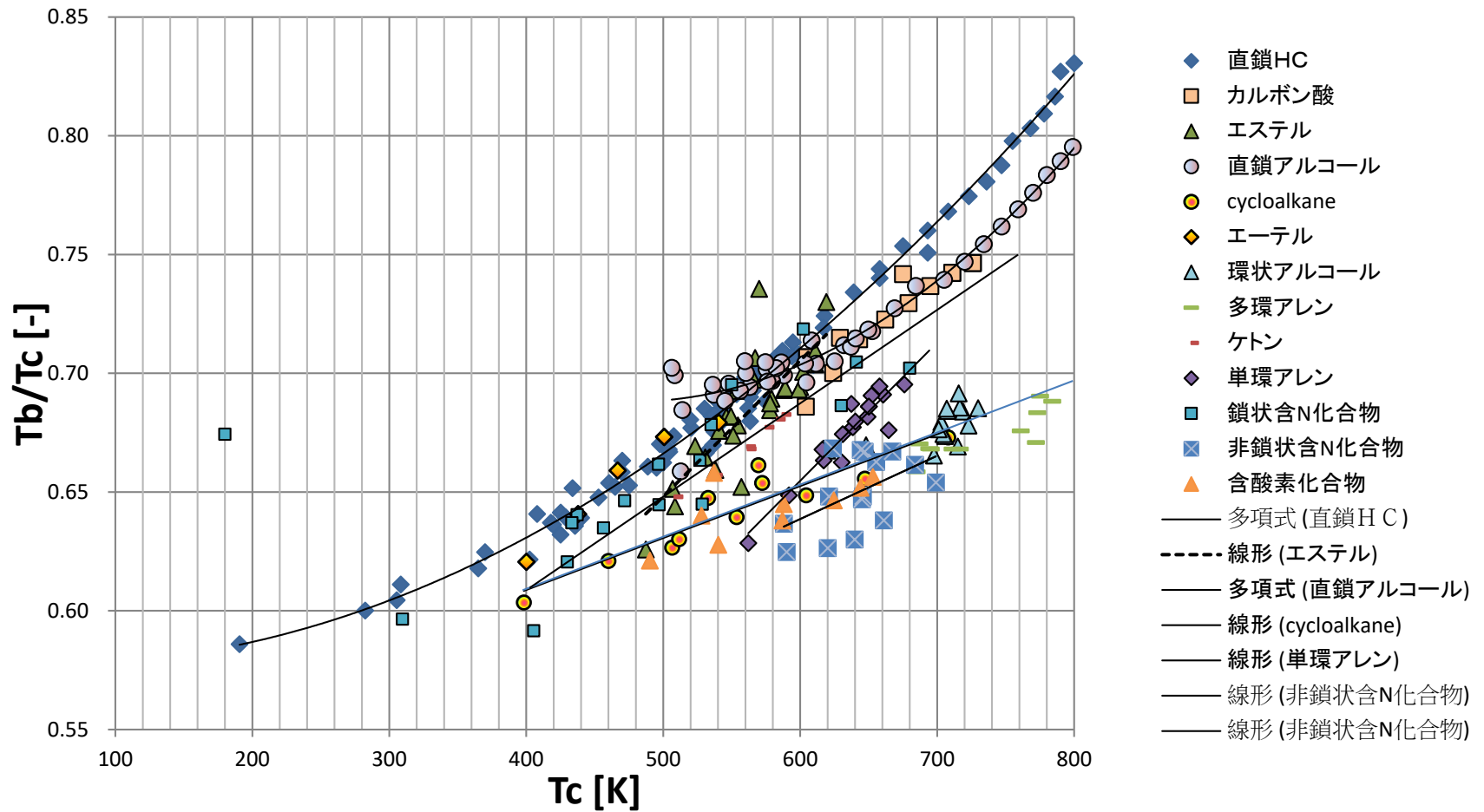
3. As ΣT_c increases,
 T_b/T_c increases
monotonically and
approches unity at
most.

- ◆ alkane
- cycloalkane
- ▲ alkene
- × alkyne
- * alcohol
- ether
- + carboxylic acid
- ketone
- ester
- ◆ halogenatedCompound
- aromatic
- ▲ N-compound
- × S-compound
- * O-compound
- Joback 相關

$$T_b/T_c = -1/(1.3 + \sum T_{ck})^4 + 0.93 = f(\sum T_{ck})$$

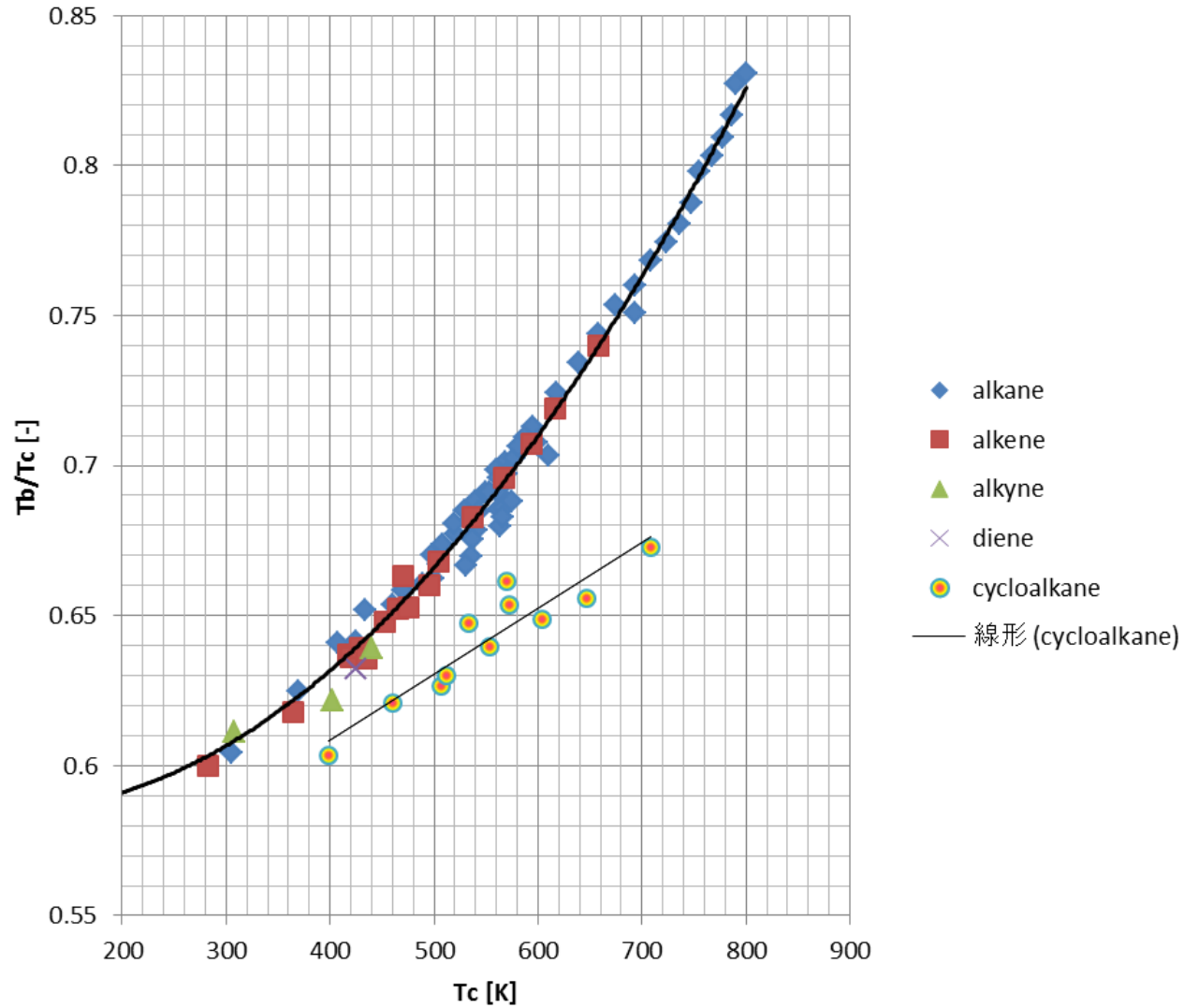


Second problem with Joback method: Tc vs. Tb/Tc

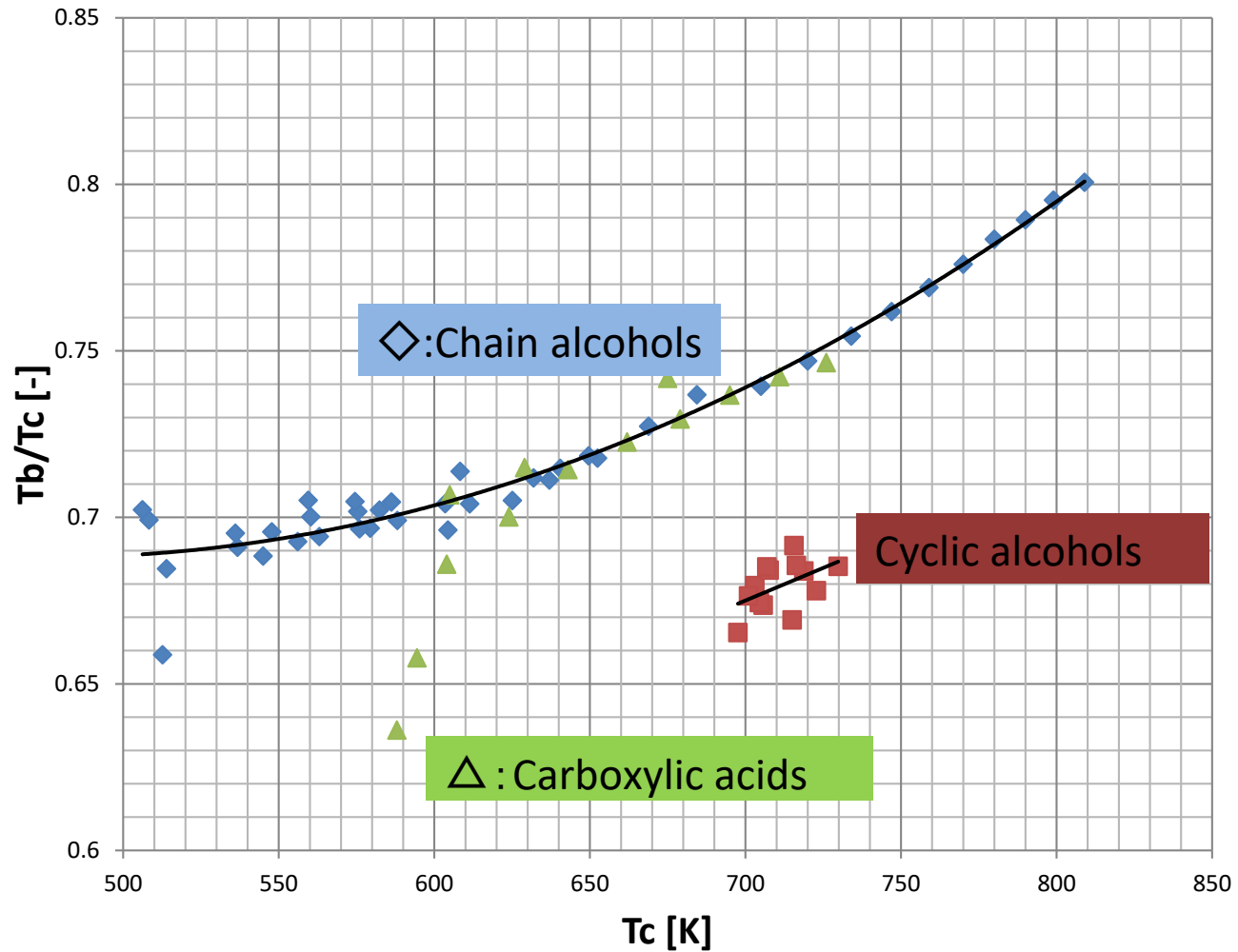


Correlation of T_b/T_c for families seems to be possible

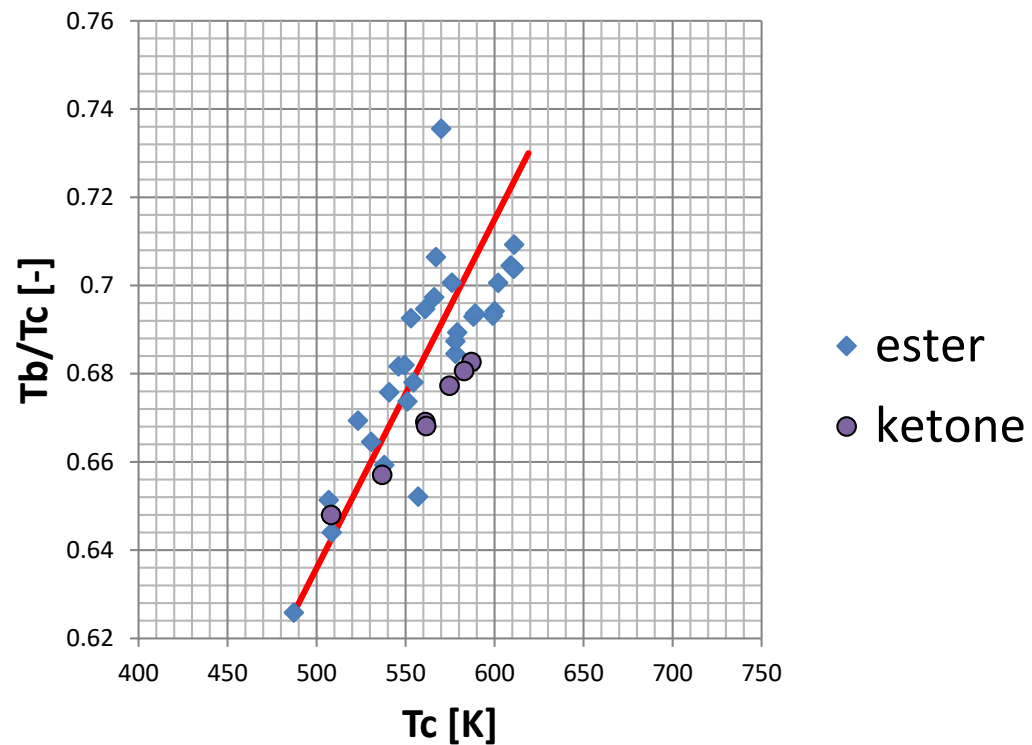
Correlation for hydrocarbons



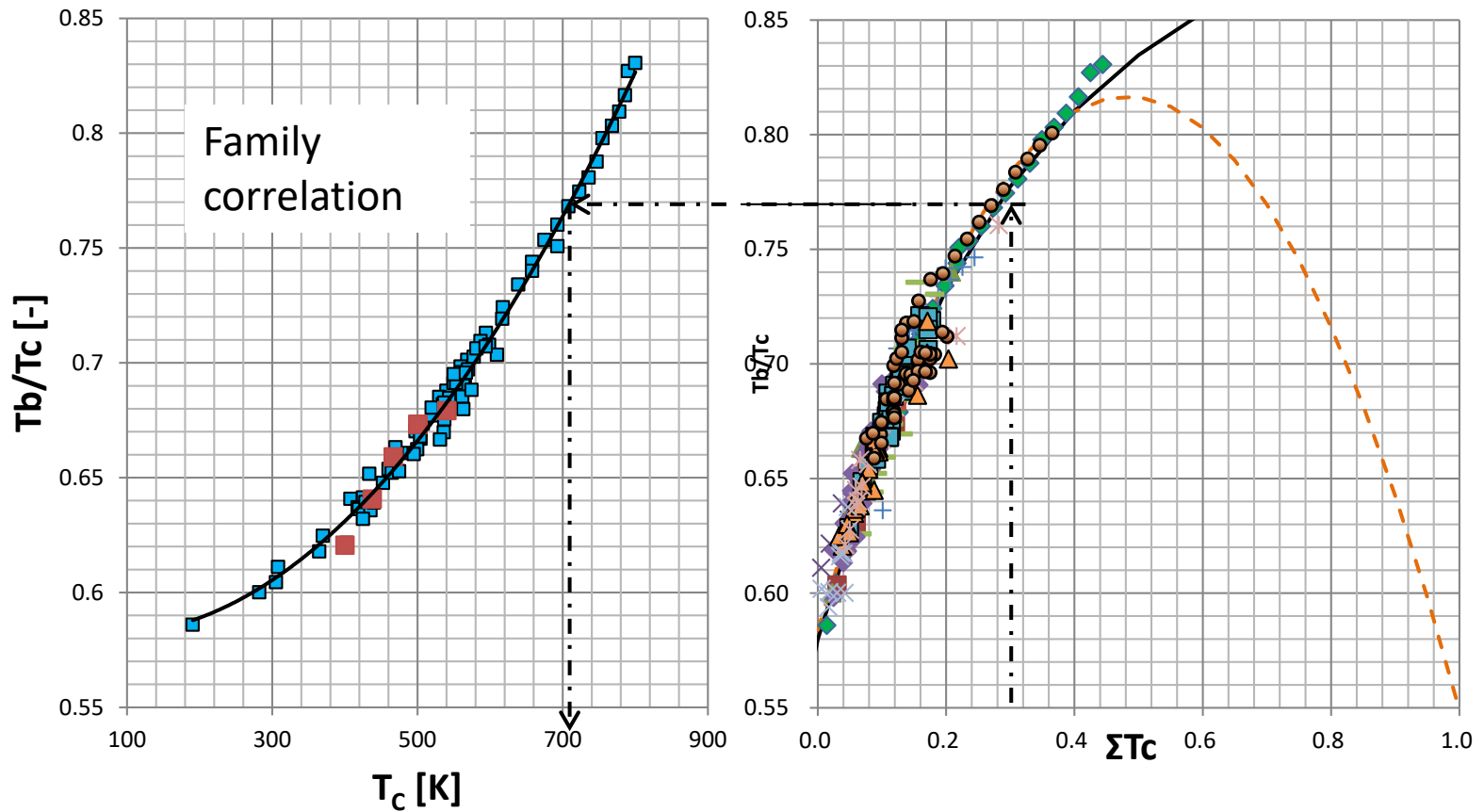
Correlation for alcohols and carboxylic acids



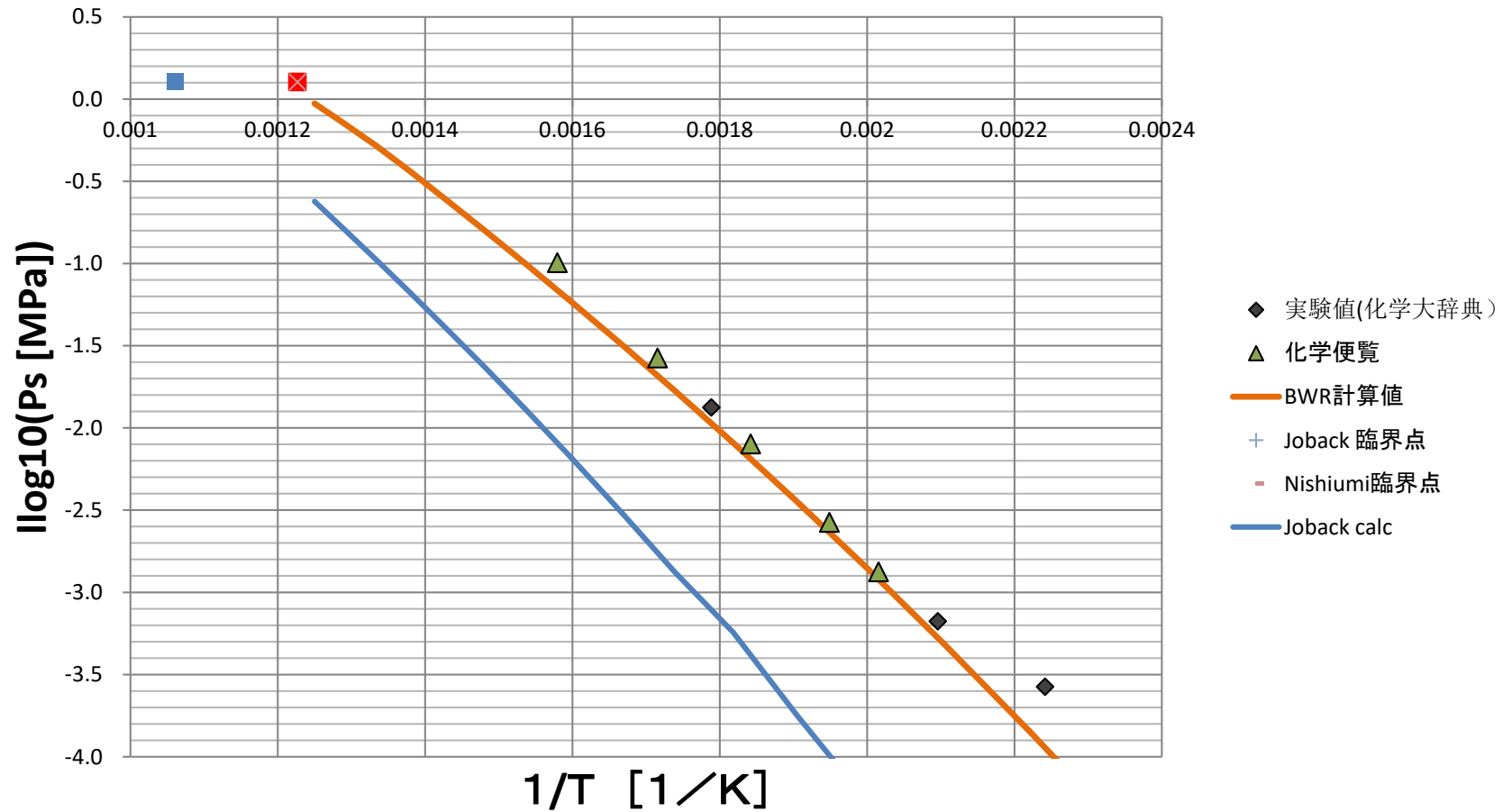
Correlation for esters and carboxylic acids



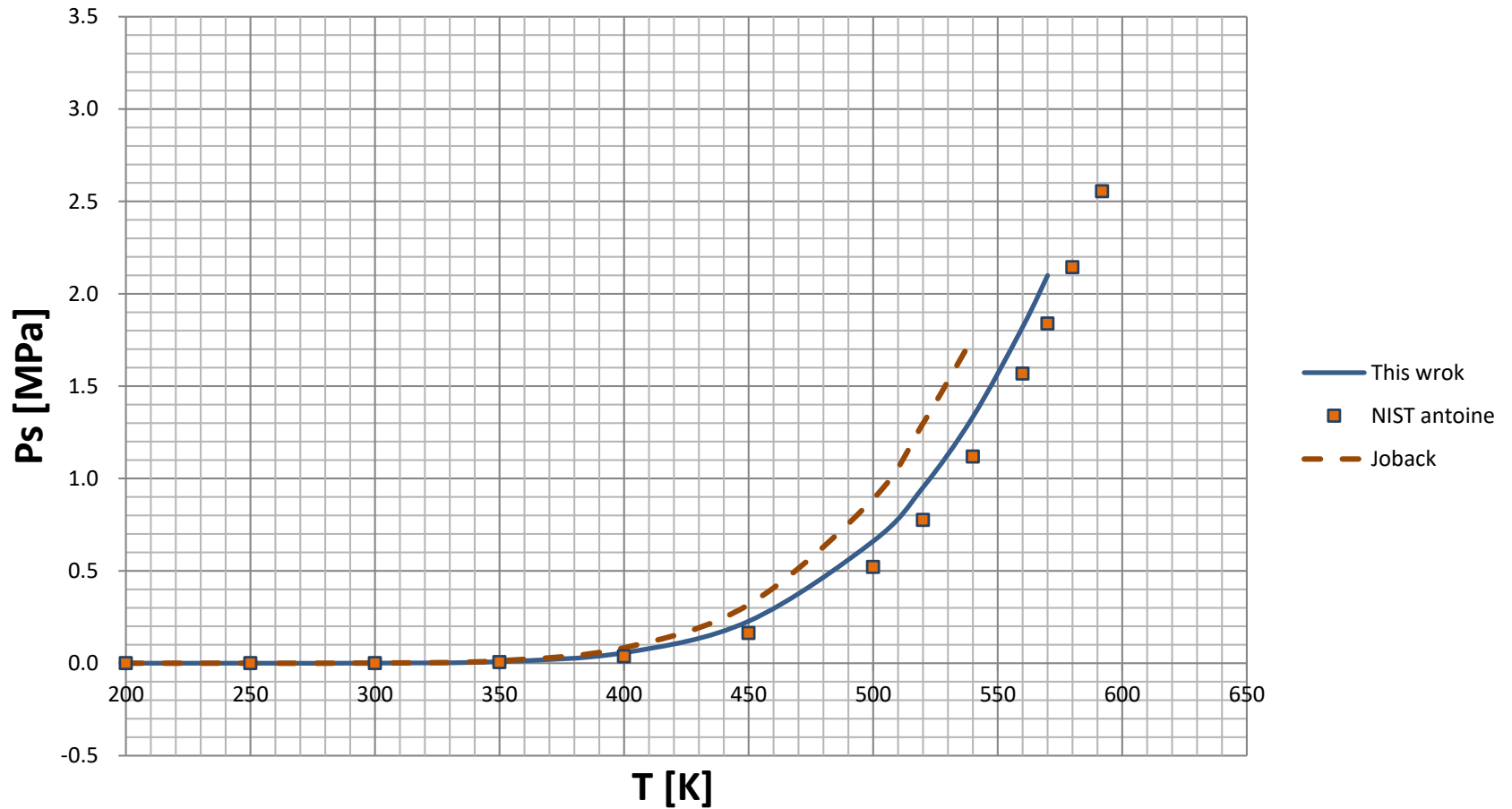
Novel method to predict T_c not using T_b directly



Vapor pressure prediction of Oleic acid



Vapor pressure of Diglyme



Liquid density prediction of Triglyme (at 1atm)

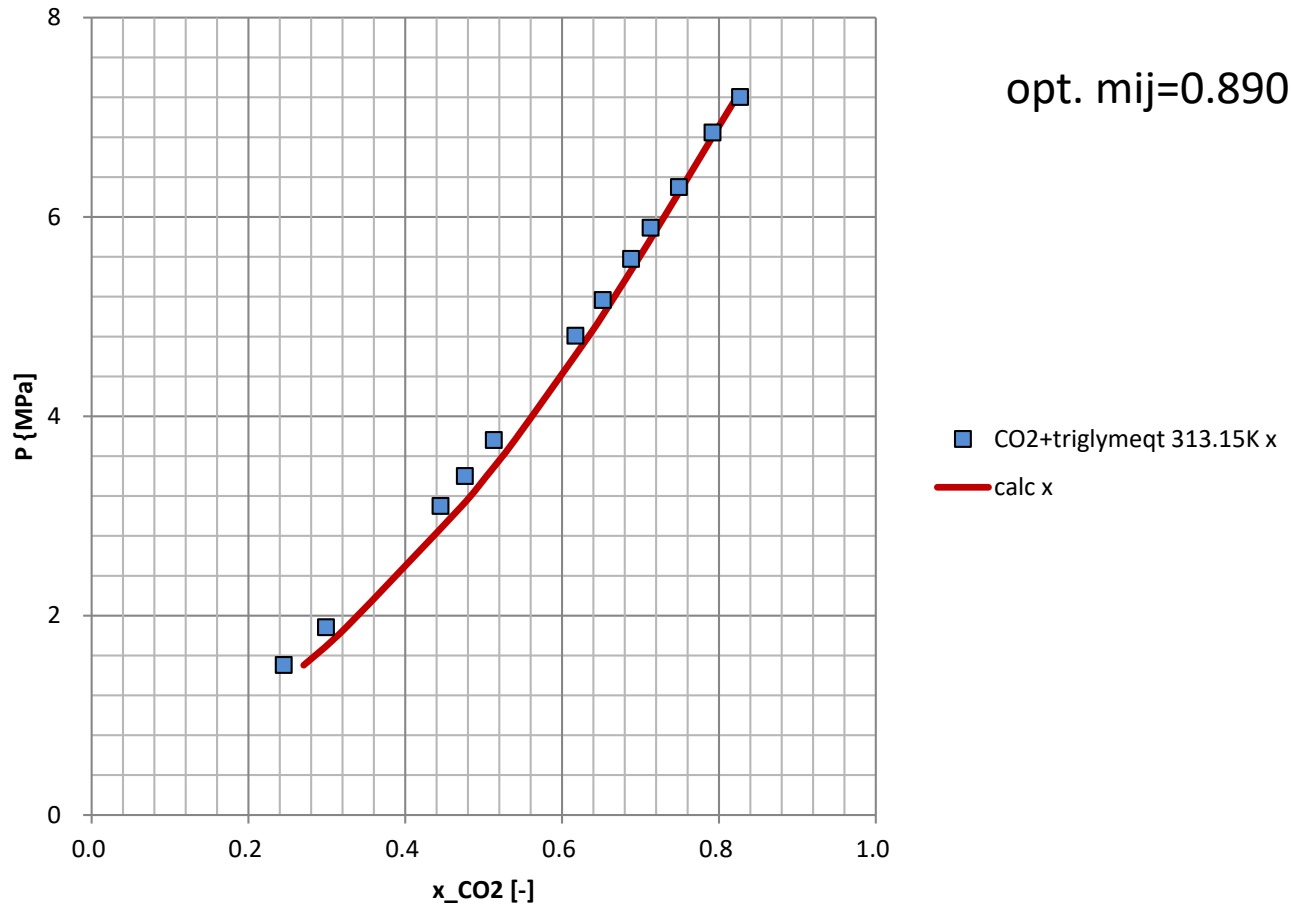
T [K]	P [MPa]	Zcal [-]	Zexp [-]	Vcal [l/g]	Vexp [l/g]	Dcal [g/l]	Dexp [g/l]	偏倚 [%]	相
273.15	0.10	0.0075	0.0079	0.0009	0.0010	1060.943	1003.990	5.67	liquid
278.15	0.10	0.0074	0.0078	0.0009	0.0010	1056.801	999.230	5.76	liquid
283.15	0.10	0.0073	0.0077	0.0010	0.0010	1052.584	994.480	5.84	liquid
288.15	0.10	0.0072	0.0076	0.0010	0.0010	1048.300	989.740	5.92	liquid
293.15	0.10	0.0071	0.0075	0.0010	0.0010	1043.955	984.980	5.99	liquid
298.15	0.10	0.0070	0.0074	0.0010	0.0010	1039.557	980.230	6.05	liquid
303.15	0.10	0.0069	0.0073	0.0010	0.0010	1035.111	975.480	6.11	liquid
313.15	0.10	0.0068	0.0072	0.0010	0.0010	1026.091	965.970	6.22	liquid
323.15	0.10	0.0066	0.0070	0.0010	0.0010	1016.927	956.440	6.32	liquid
333.15	0.10	0.0065	0.0069	0.0010	0.0011	1007.644	946.890	6.42	liquid
343.15	0.10	0.0063	0.0068	0.0010	0.0011	998.255	937.300	6.50	liquid
353.15	0.10	0.0062	0.0066	0.0010	0.0011	988.772	927.690	6.58	liquid
363.15	0.10	0.0061	0.0065	0.0010	0.0011	979.199	918.020	6.66	liquid

Abs.Avg.Deviation **6.2**

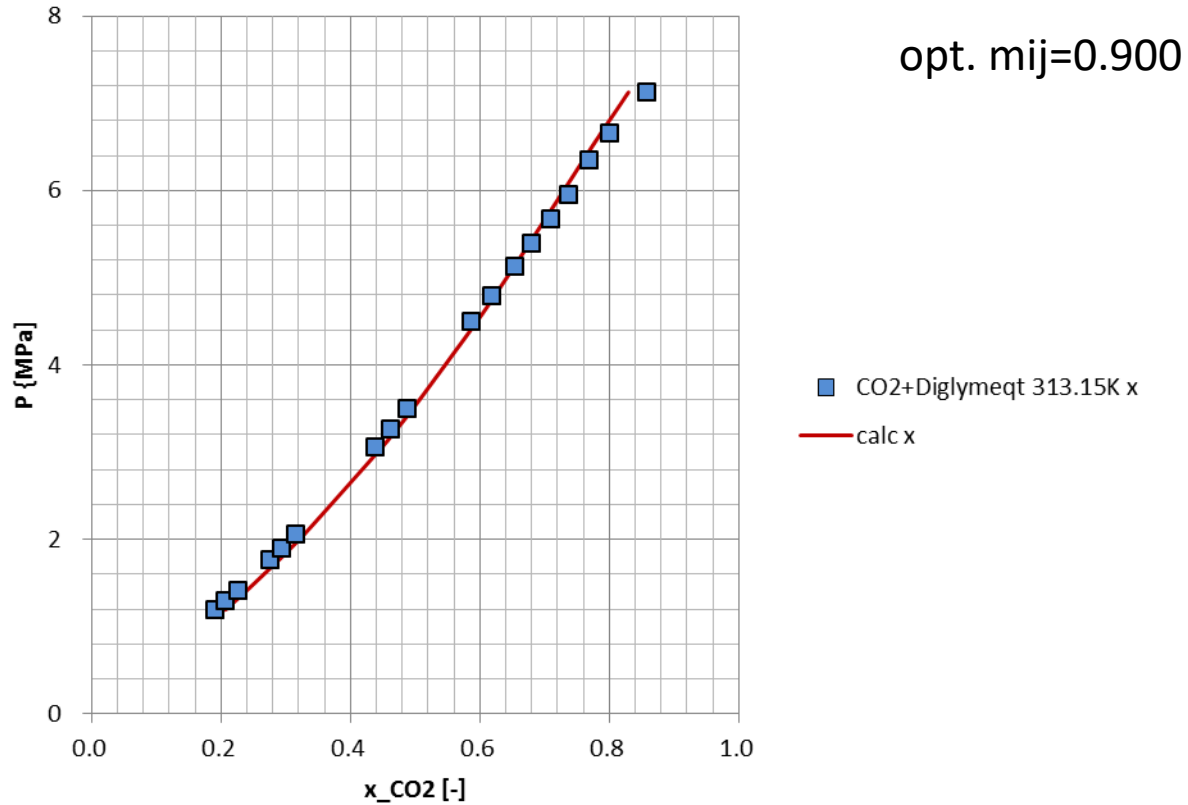
Data point: 13

$$\text{Dev.}[\%] = 100 \times (\text{calc.} - \text{exptl.}) / \text{exptl}$$

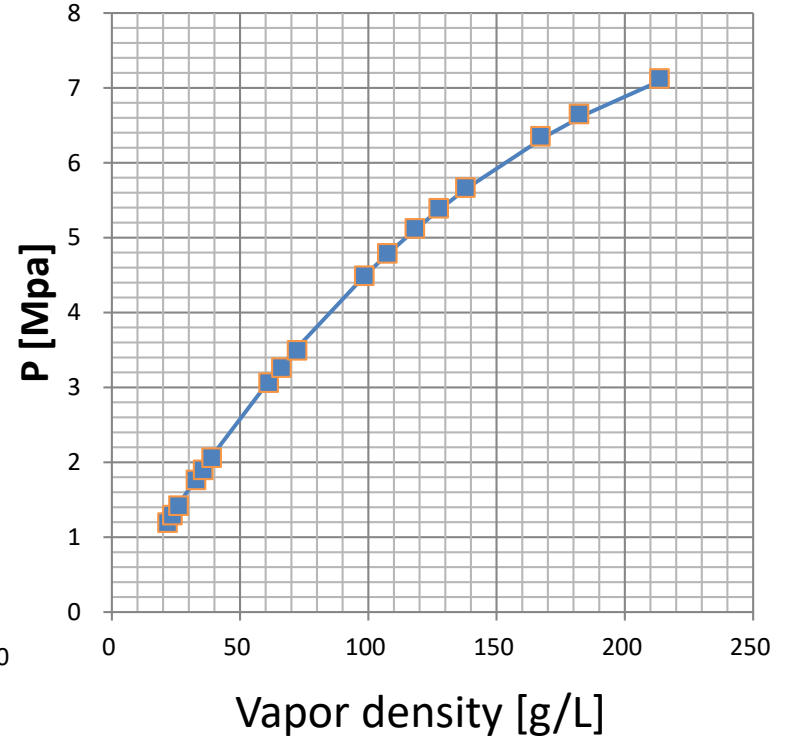
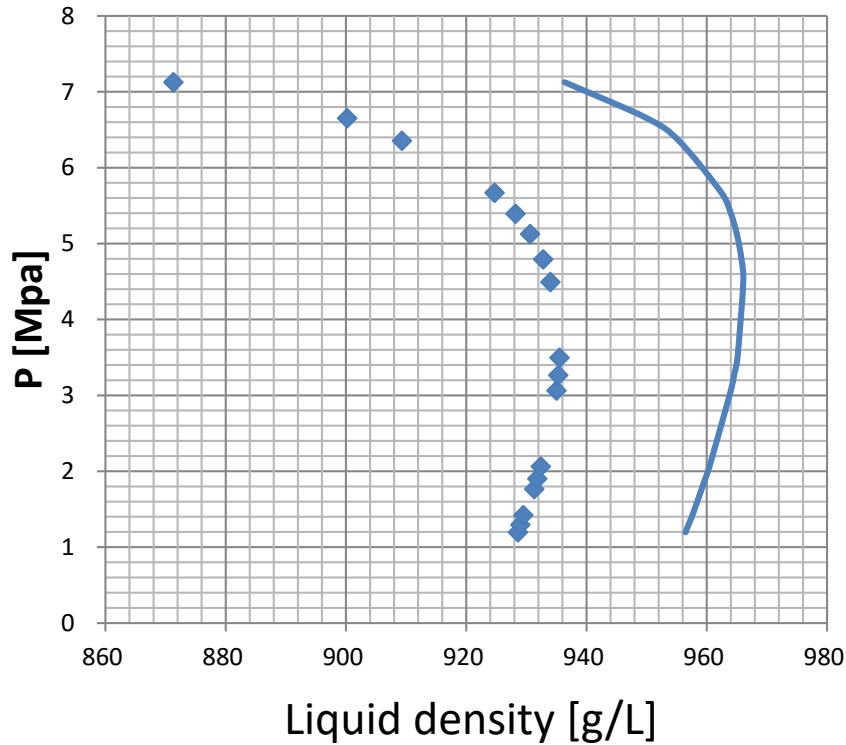
CO₂-Triglyme系の溶解度 313.15K



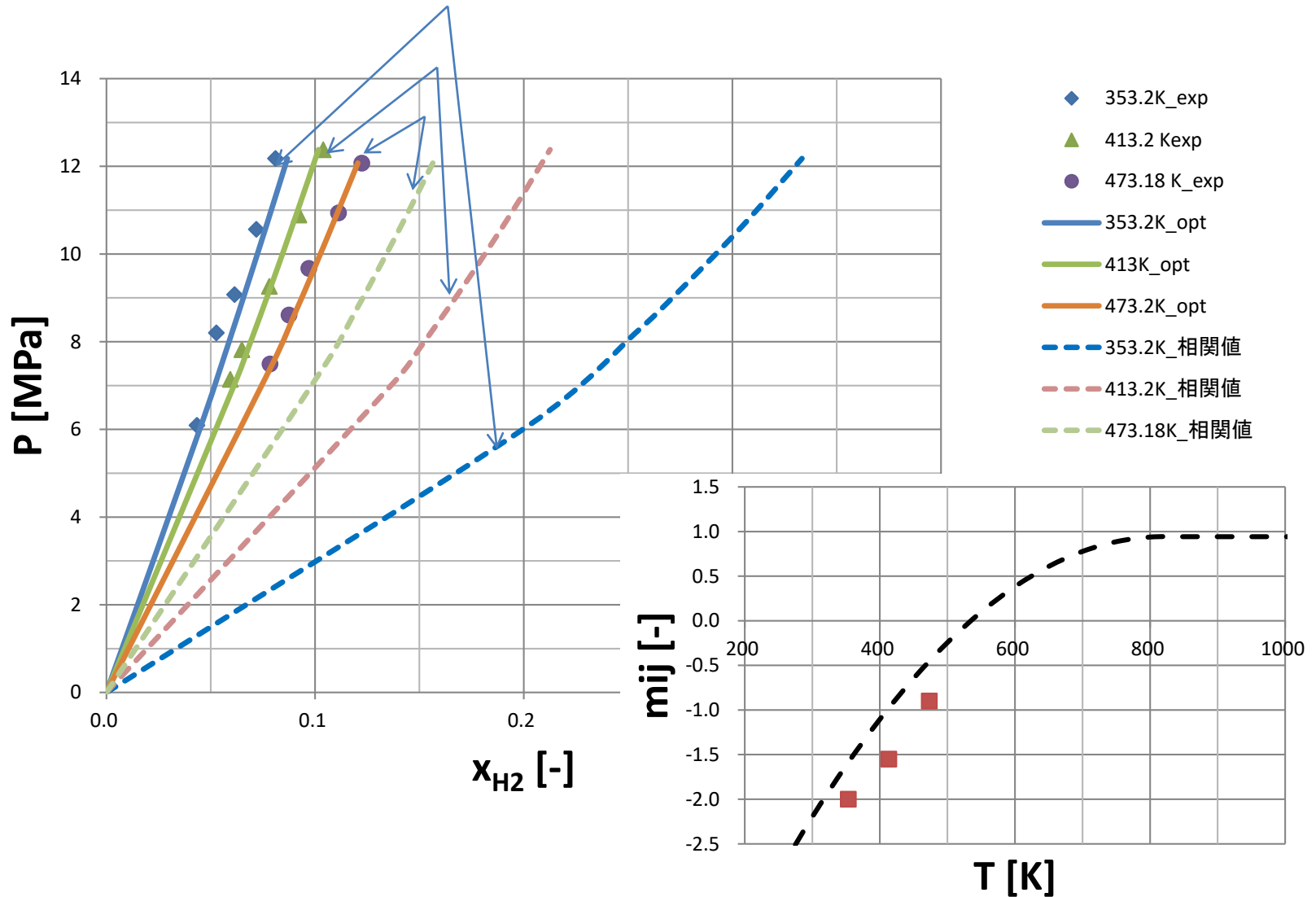
Solubility of CO₂-Diglyme at 313.15K



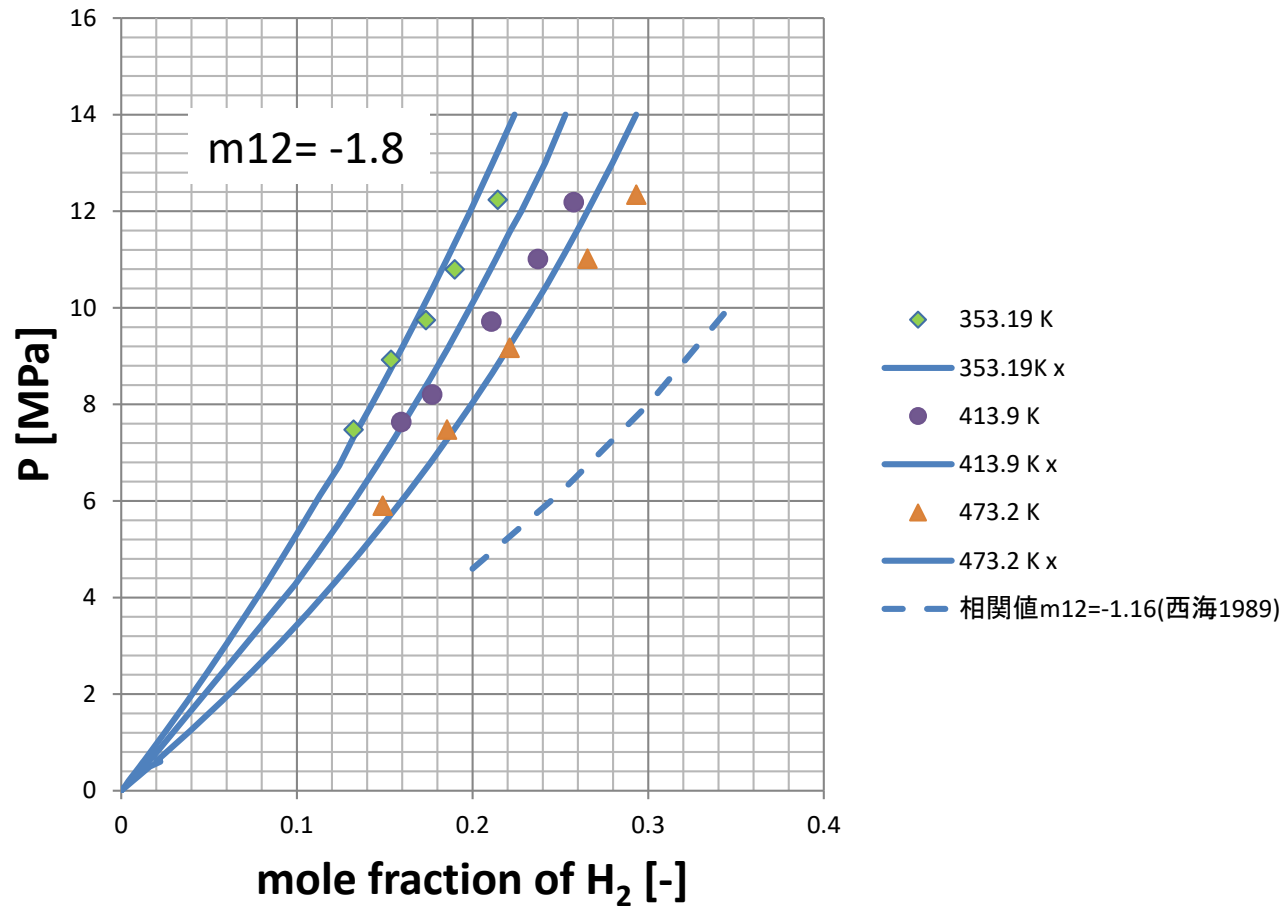
Saturated density of CO₂+Diglyme system



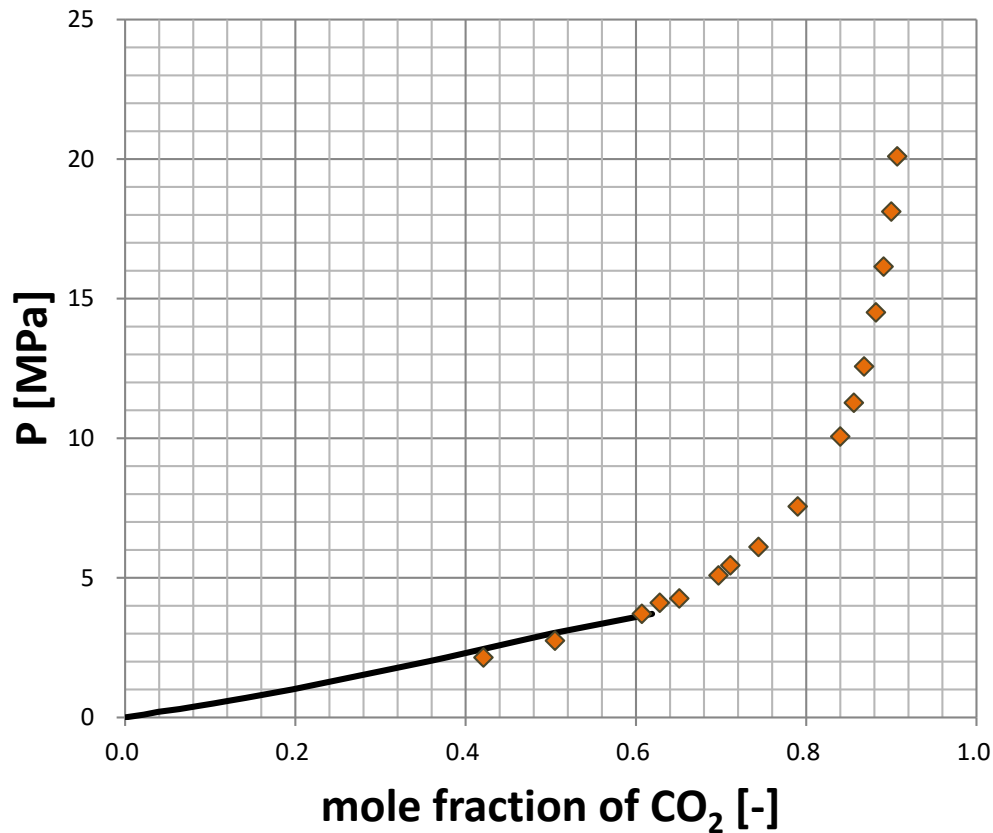
Solubility of H₂ in Oleic Acid



Solubility of H₂ in Triolein



Solubility of CO₂ in PAG-1 at 344.5K



opt. mij =0.60

Converged
under 3.7 MPa

Prediction of Tc and Results

	Digyme	Triglyme	Tetraglyme	Oleic acid	Triolein	PAG-1
分子量	134	178	222	282	885	1105
Tc(this work) [K]	592	652	698	(Caroxylic acid) 943	(Ester) 835	(Ether) 910
Tc(Joback) [K]	570	636	703	8152	4019	8541
Vapor pressure	better			better		
Liq. density at 1atm	2.8%	6.2%	9.0%			
Solubility of H ₂ Opt. mij				Excellent temp. dependent -1~-2	Excellent -1.8	
Solubility of CO ₂ Opt. mij	0.900	0.890	0.845		Excellent temp. dependent -0.8	0.6
Sat. Liquid density	3.8%	6.5%	8.4%			
Sat. vapor density	0.9%	1.1%	1.1%			

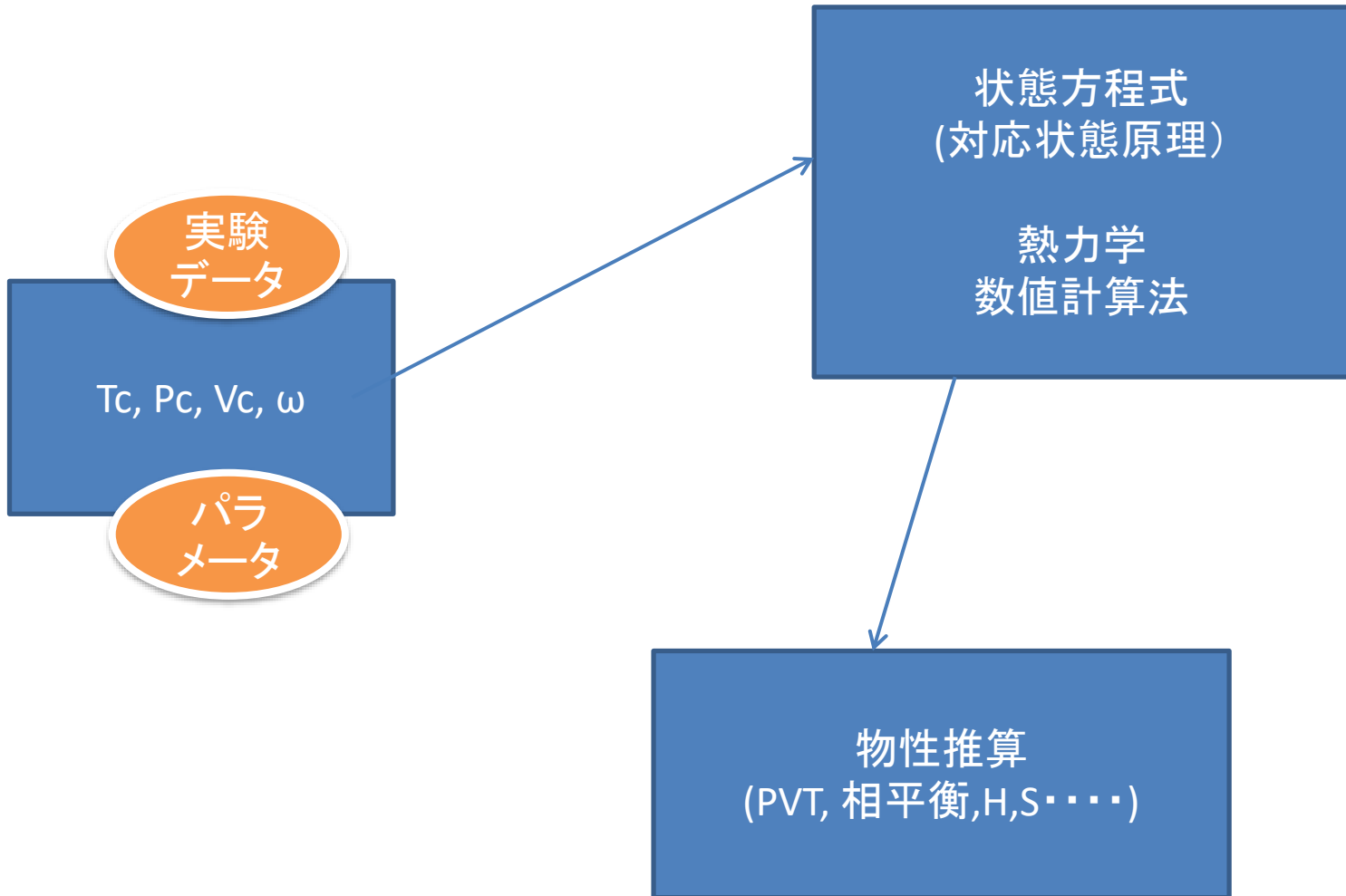
Conclusion

- Extending the Joback correlation to a big molecule has failed. Instead boiling point prediction, relationship between T_c and T_b/T_c depending family component seems effective.

ご清聴を感謝します

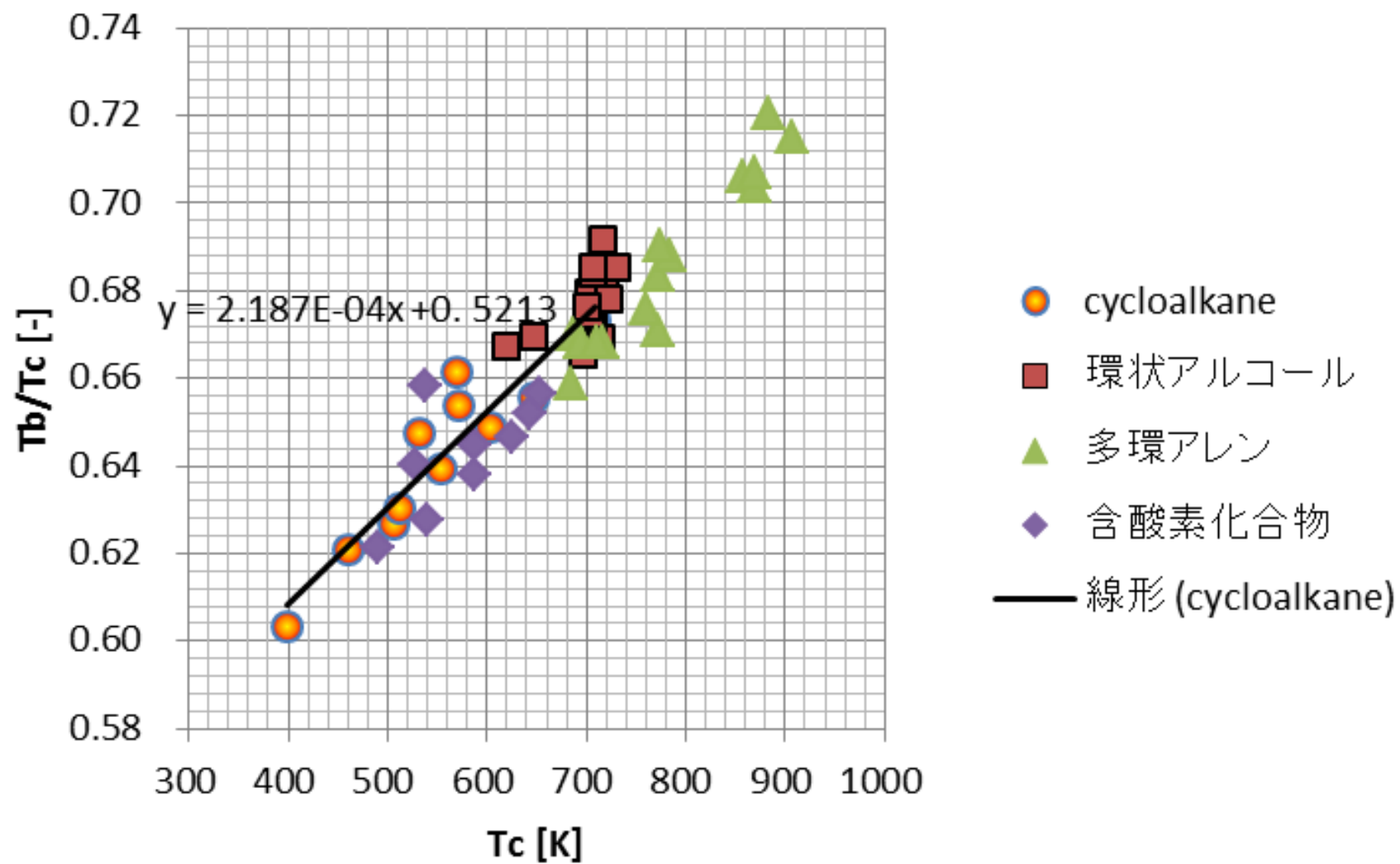
ご清聴を感謝します

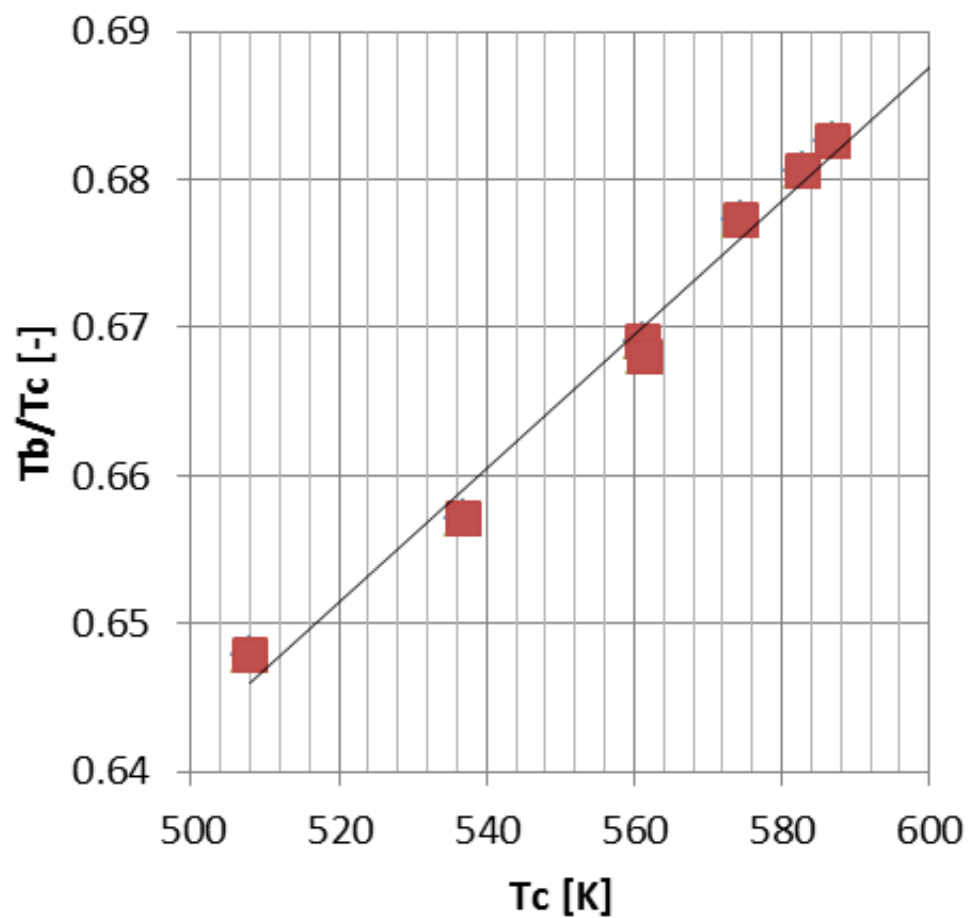
内挿的推算法と外挿的推算法



これからの問題

- 大きな分子での V_c の線形性をどう考えるか。
剛体球モデル的に考えればOK
- 大きな分子での P_c の線形性をどう考えるか。
 $Z_c = P_c V_c / R T_c = 0.29$ あたりの検討





▲ ケトン

◆ ケトン(全点)

■ ケトン(異常点削除)

— 線形(ケトン(異常点削除))

偏心係数

$$\log P = A - \frac{B}{T}$$

$$W = -\log_{10} \frac{(P^S)_{T_r=0.7}}{P_c} - 1$$

(T_c, P_c), ($T_b, 1 \text{ atm}$)の
2点からClausius-
Clapeyron式により蒸
気圧式が得られる。そ
れより w が求められ
る

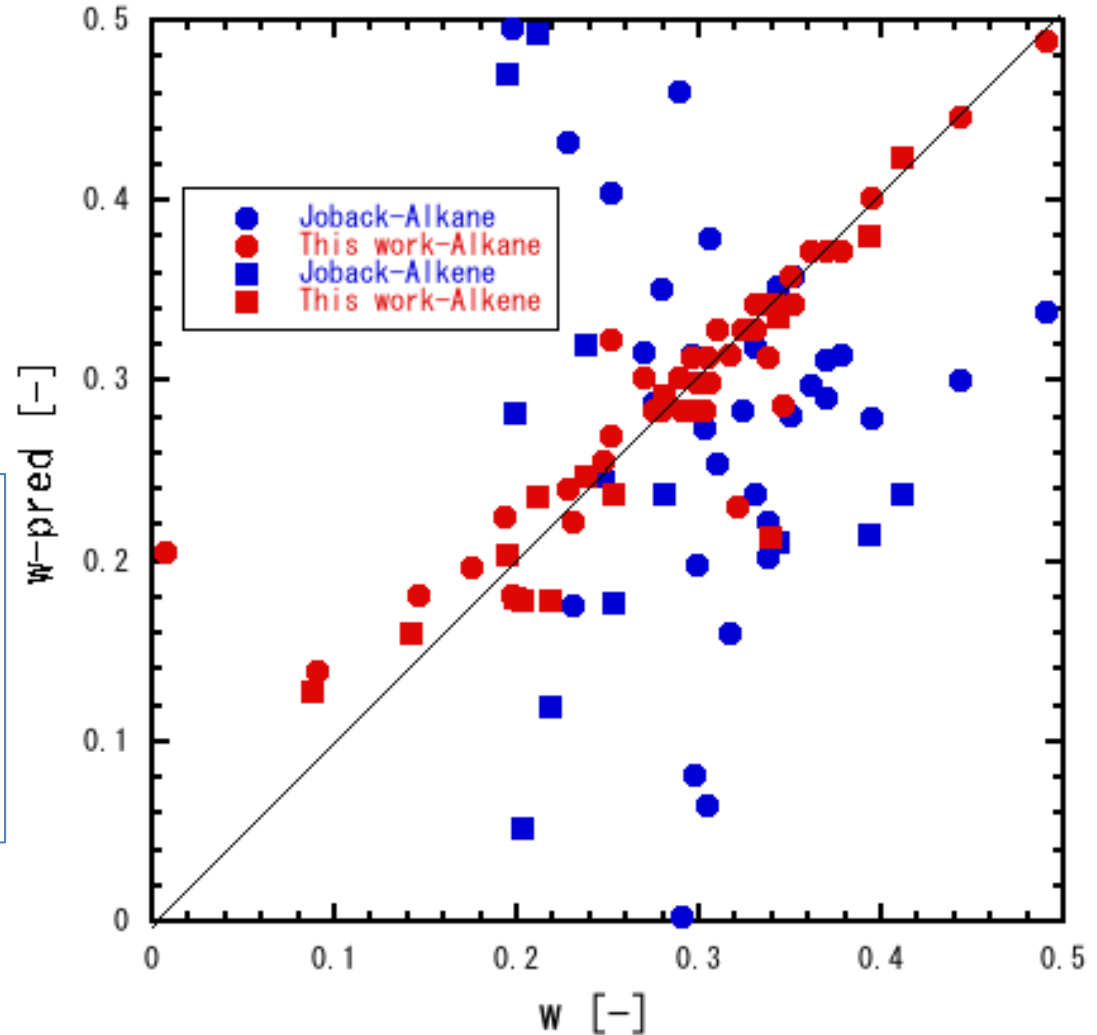


Fig. Prediction of acentric factor (Red: This work, Blue: Joback)

蒸気圧計算

基本物性パラメータが決まればEOSを用いて諸物性を推算できる。

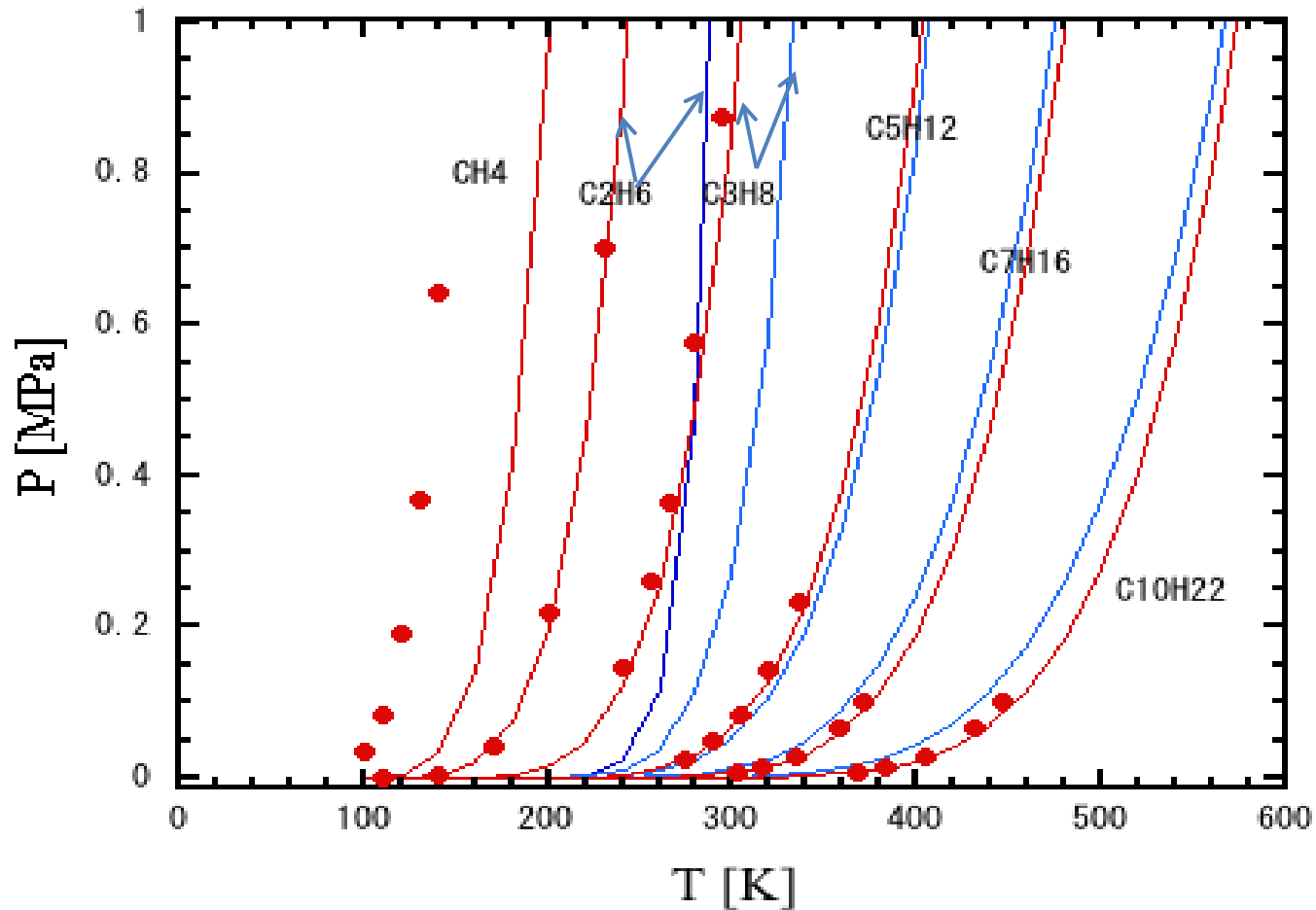
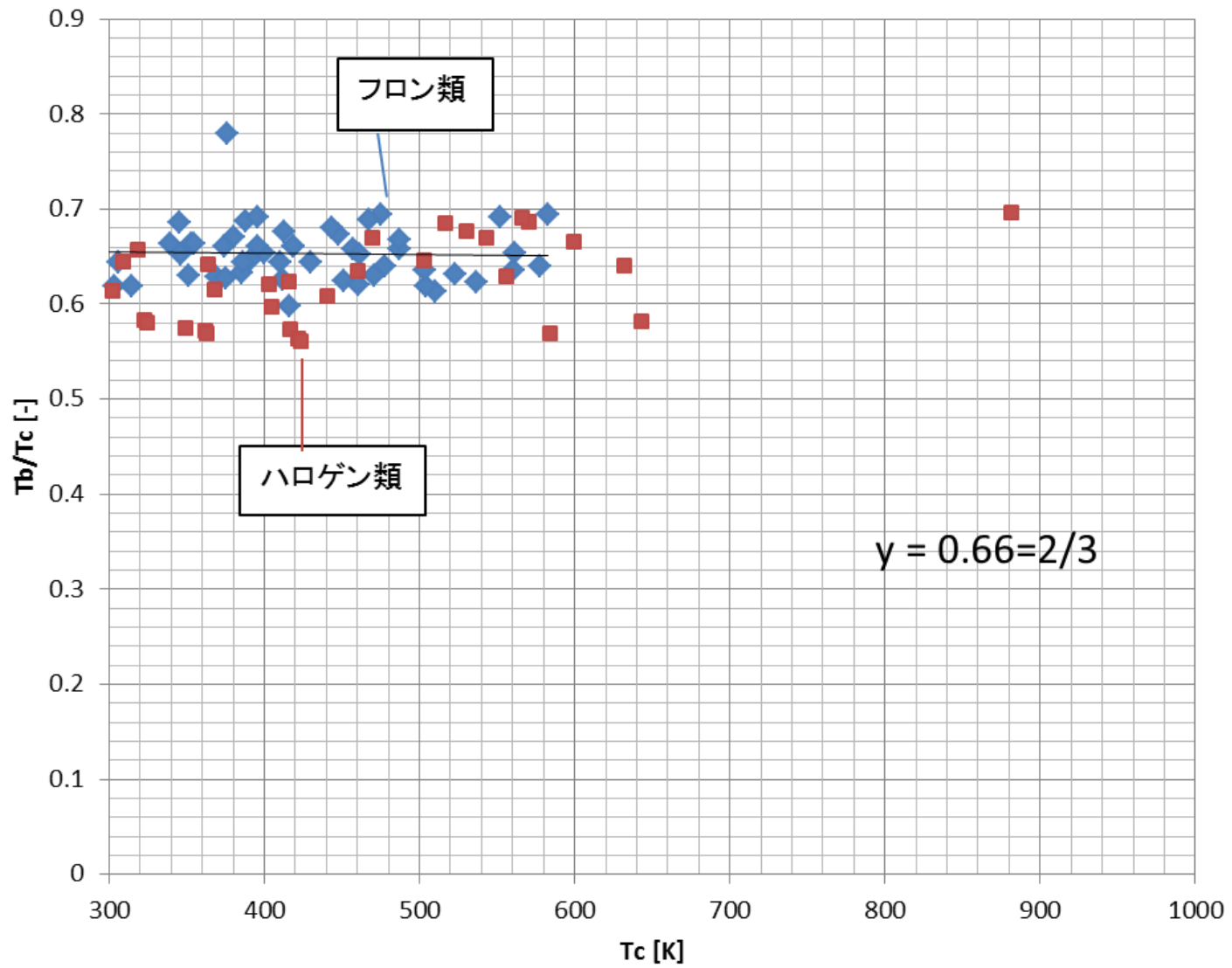
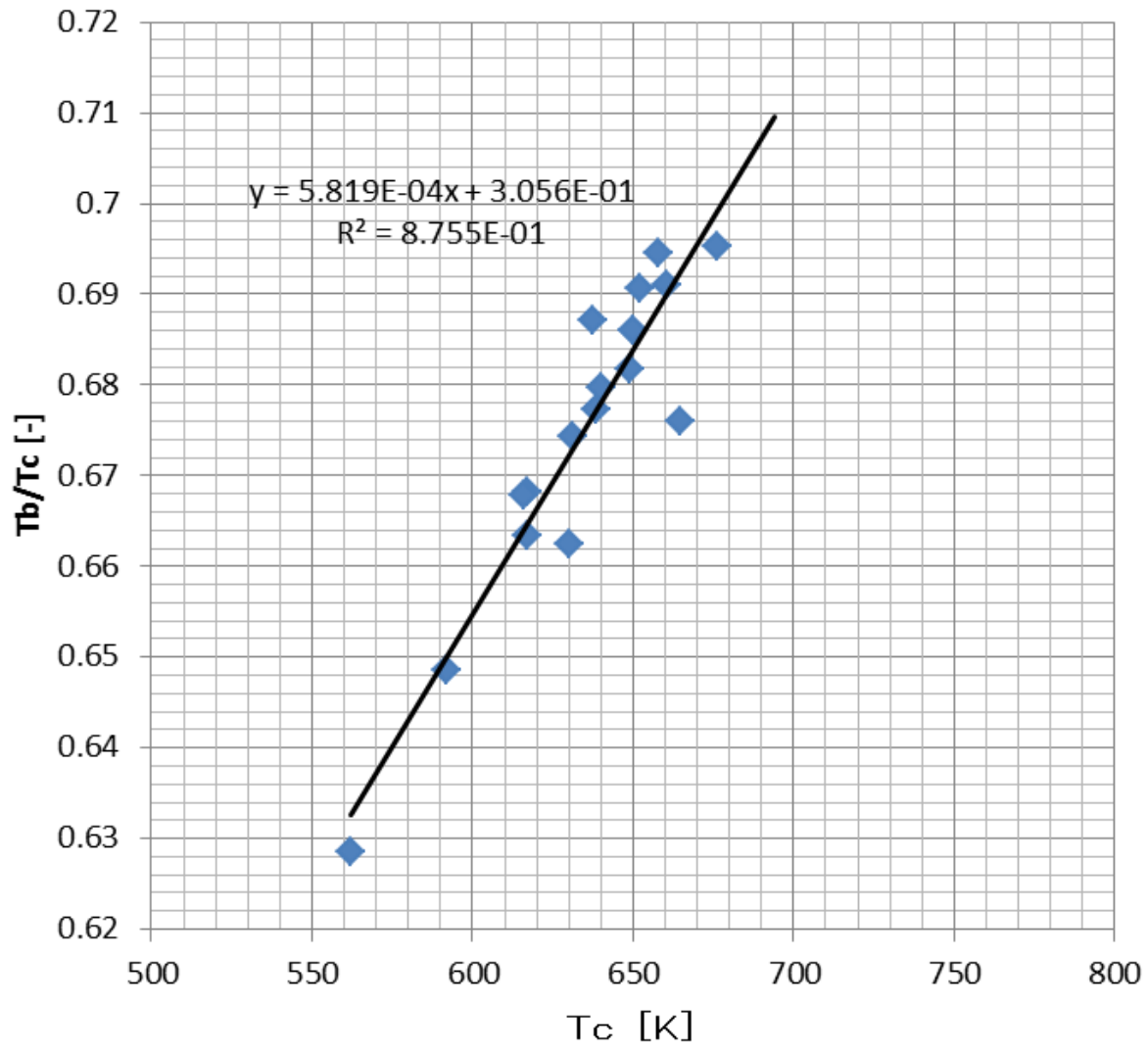
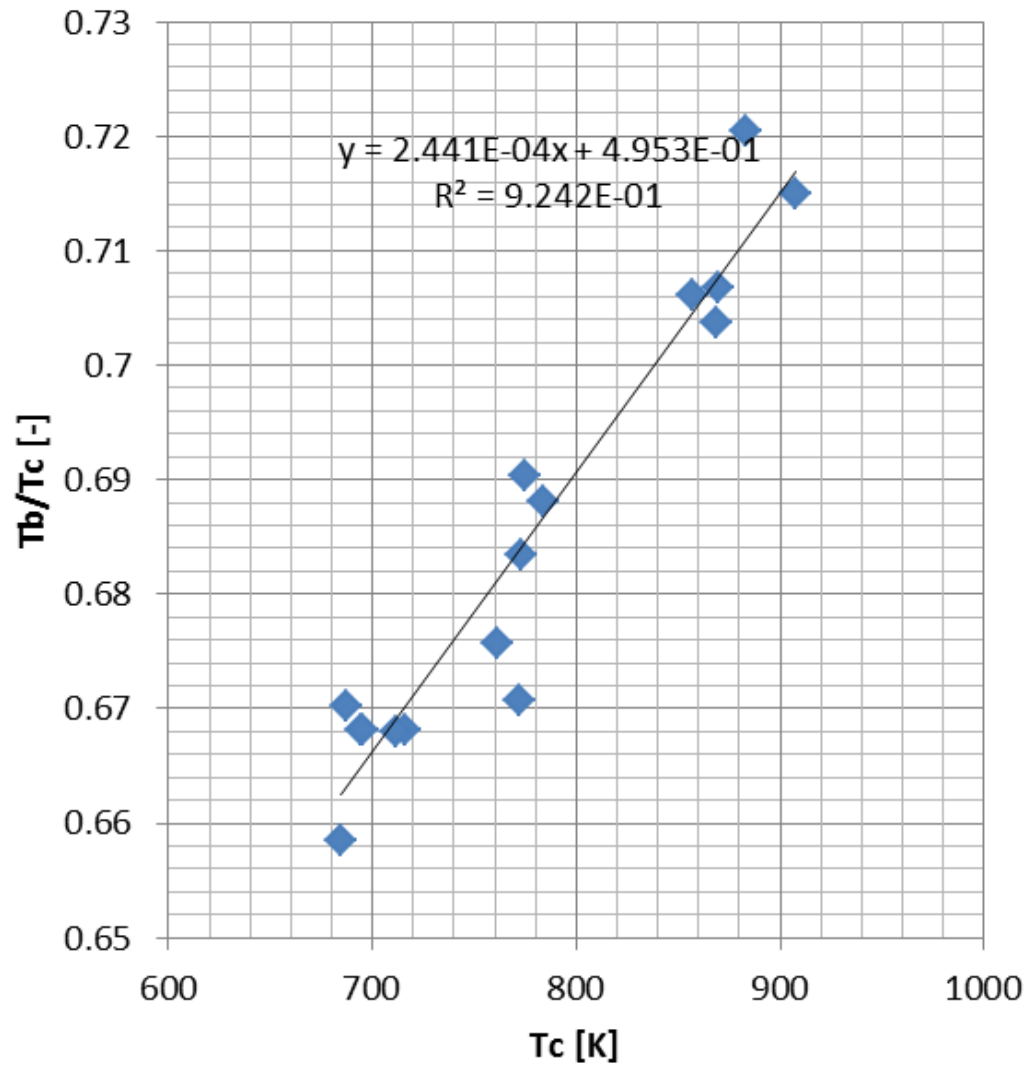


Fig. Prediction of vapor pressure (Red: This work, Blue: Joback)



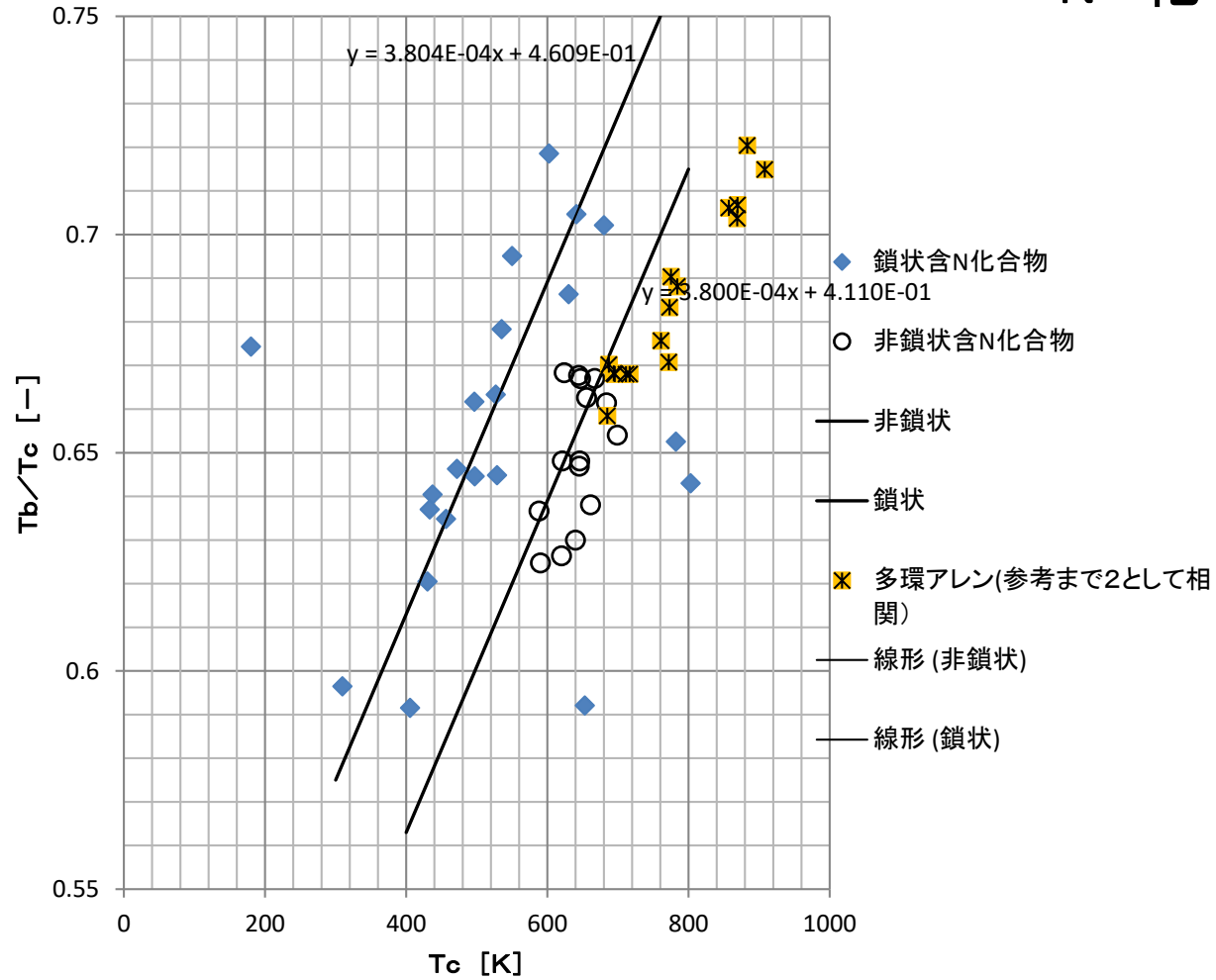


- ◆ 単環アレン
- 線形(単環アレン)

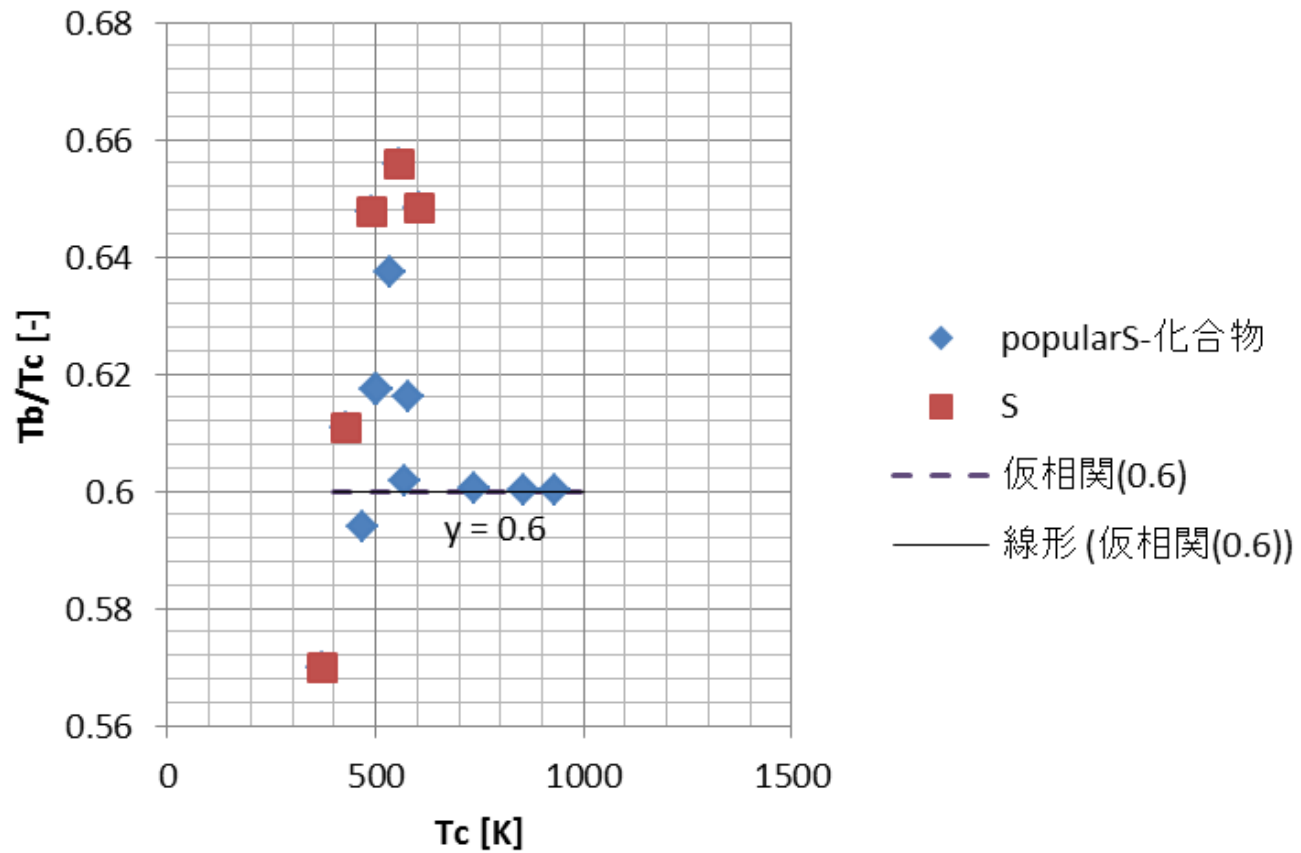


- ◆ 多環アレン
- 線形(多環アレン)

N 化合物



S 化合物



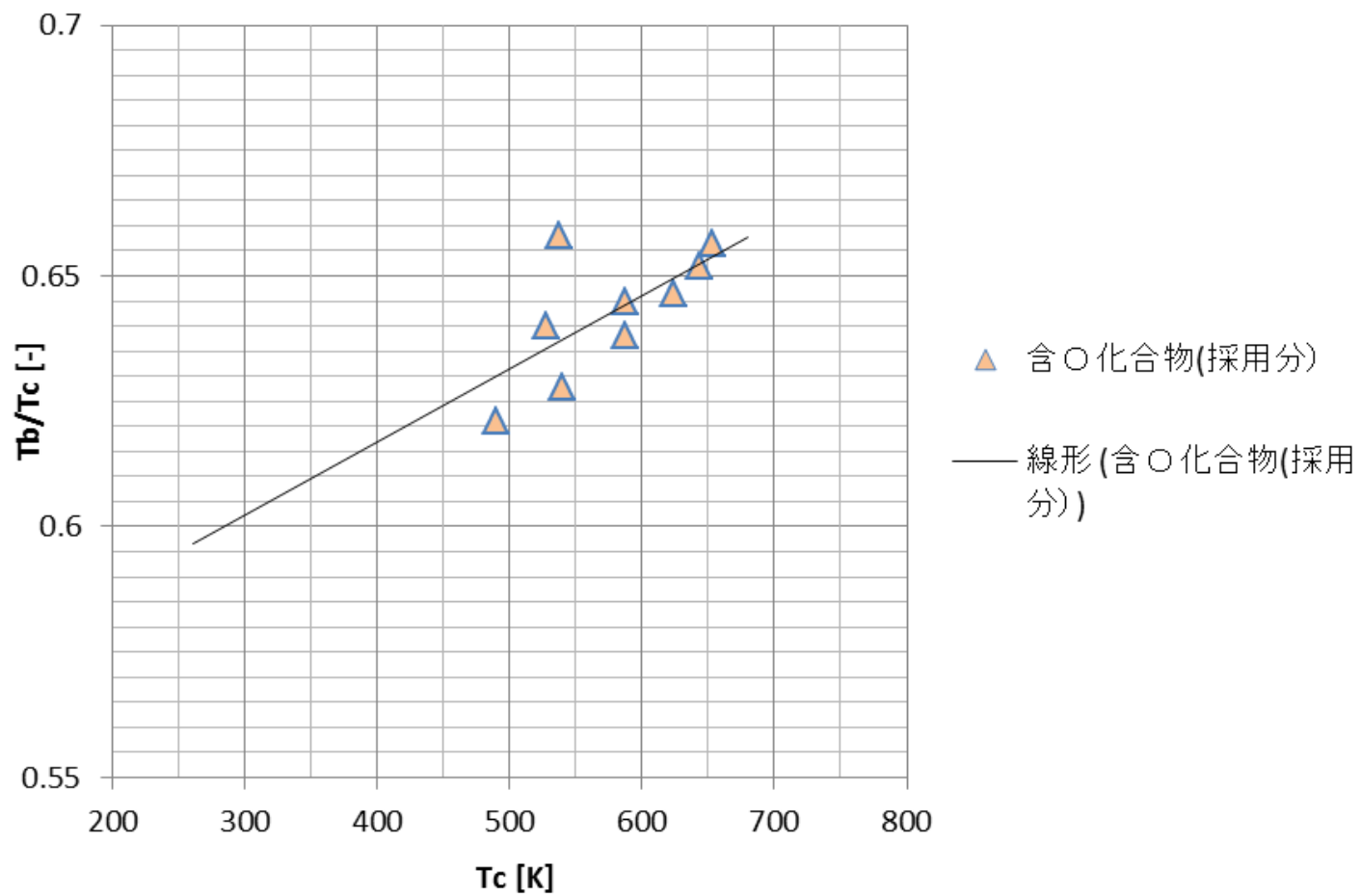
ファミリー相関 $T_b/T_c = g(T_c)$

1. 直鎖HC(alkane/alkene/alkyne/diene)・エーテルは一致性が高い。
 $T_b/T_c = 4.639E-07 * T_c^2 - 6.783E-05 * T_c + 0.5840$ ($T \geq 280K$)
2. シクロアルカン・環状アルコール・多環アレン・含酸素化合物(仮相関)
は、 $T_b/T_c = 2.187E-04 * T_c + 0.5213$
3. カルボン酸と直鎖アルコールは一致すると考えてよい。
 $T_b/T_c = 1.021E-06 T_c^2 - 9.724E-04 T_c + 9.197E-01$ ($T \geq 400K$)
4. エステル・ケトンは、 $T_b/T_c = 7.904E-04 * T_c + 0.2407$
5. フロン類・ハロゲン化物は $T_b/T_c = 2/3 = 0.6667$
6. 単環アレンは $T_b/T_c = 5.819E-04 * T_c + 0.3056$
7. 鎖状含N化合物は $T_b/T_c = 3.804E-04 * t_c + 0.4609$
8. 非鎖状含N化合物は $T_b/T_c = 3.800E-04 * T_c + 0.4110$
9. S化合物 $T_b/T_c = 0.60$ (仮相関)
10. O化合物 $T_b/T_c = 2.000E-04 * T_c + 0.5250$ (仮相関)

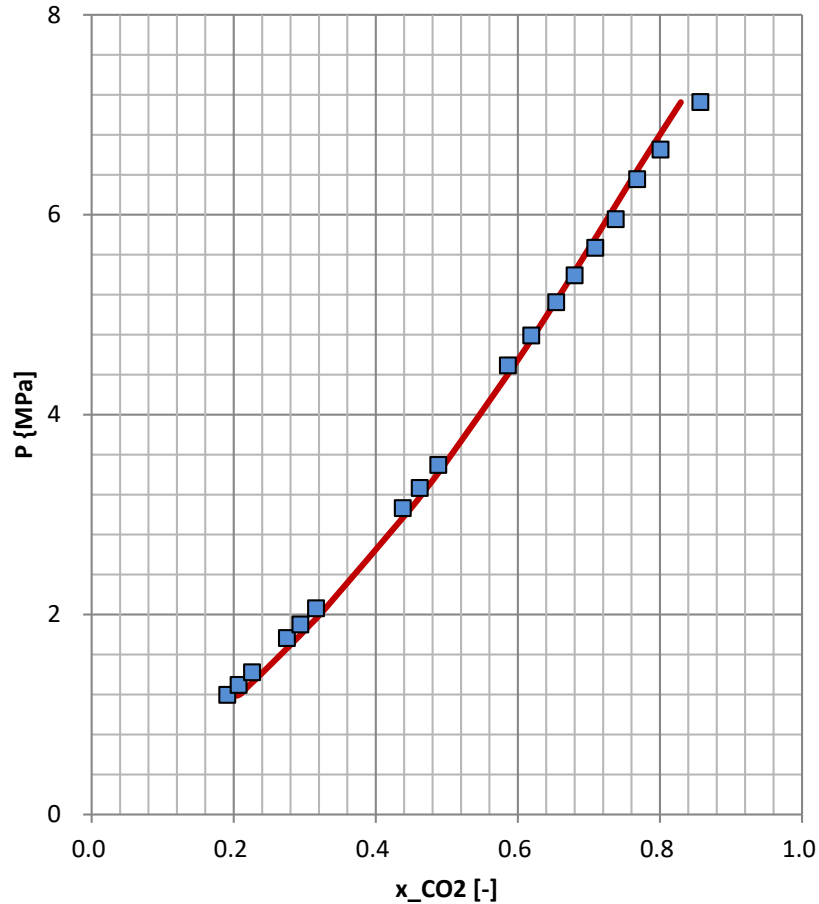
ファミリー法による T_c の推算

- T_b は $\sum T_{bk}$ に線形なため大きな分子では大きな値となり、結果 T_c の推算値が大きくなりすぎ実用的でない
 - 1. $T_b/T_c = -1/(1.3 + \sum T_{ck})^4 + 0.93 = f(\sum T_{ck})$
 - 2. ファミリー相関 $T_b/T_c = g(T_c)$
- を得た。
- $\sum T_{ck} \rightarrow (T_b/T_c) \rightarrow T_c$
- と T_b を経ずに T_c を推算できる方法を提供する

O 化合物



CO₂-Tetraglyme系の溶解度 313.15K



opt. mij=0.845

■ CO2+Diglymeqt 313.15K x
— calc x