Solutions for R&D to Design

Estimation of Vapor-Liquid Equilibrium from Liquid-Liquid Equilibrium Data

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PreFEED Corporation

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Introduction

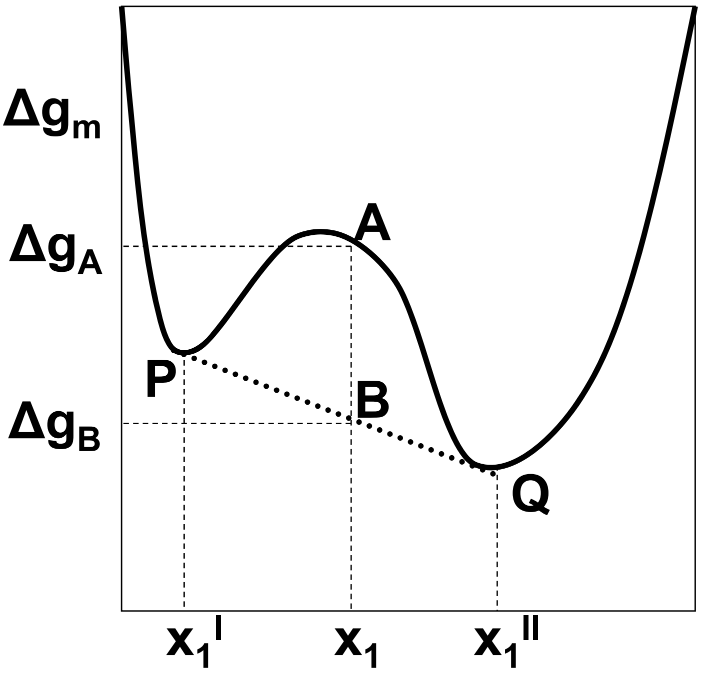
First, we introduced a vapor-liquid equilibrium estimation method from azeotropic data as an estimation method of vapor-liquid equilibrium in the absence of measured values (Tips #1109).

Here, we will introduce a vapor-liquid equilibrium estimation method when liquid-liquid equilibrium data can be used. The liquid-liquid equilibrium data is usually in a lower temperature region than the vapor-liquid equilibrium.

Basic Theory of Liquid-Liquid Equilibrium

Whether the liquid phase stably exists in one phase or whether it is separated into two phases is a great concern not only in reaction processes but also in separation processes. It is said that an unfavorable foaming phenomenon occurs when a liquid phase is separated into two phases in a distillation column. On the other hand, in an extraction process, two liquid phases must be stably formed.

The formation of two liquid phases will depend on the free energy change of mixing in a multicomponent system. When two liquid phases are brought into contact with each other, a single liquid phase will form as long as dissolving one liquid phase into the other is more stable in terms of energy.



Suppose now that there is a liquid phase with a composition x_1, and that the free energy change of the mixture is given at point A.

The straight line PQ is a tangent to the free energy change curve. When comparing the points A and B, point B has a lower energy and is stable. Therefore, the liquid phase is separated into two liquid phases having compositions of x_1^I and x_1^{II}. The quantitative ratio between phase I and phase II is given by the ratio BQ: BP.

Mathematically, if the second order derivative of the free energy change curve of mixing is > 0, there is no concavity so liquid-liquid phase separation does not occur.

Free Energy Change due to Mixing

$$\Delta g_m = g_{mixture} - (x_1 g_{pure1} + x_2 g_{pure2})$$

$$= g^E + RT(x_1 \ln x_1 + x_2 \ln x_2)$$

$$= RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) + RT(x_1 \ln x_1 + x_2 \ln x_2)$$

$$= RT[x_1 \ln(\gamma_1 x_1) + x_2 \ln(\gamma_2 x_2)]$$

- If Δg_m has a concave portion on a curve, phase separation always occurs, so it is possible to judge phase separation by drawing a curve with an activity coefficient model and checking concavities and convexities.
- In certain activity coefficient models liquid-liquid equilibrium cannot be represented, because concavities cannot be expressed regardless of the parameter values.

- Liquid phase stability condition:
  (The free energy change curve of the mixture is convex downward) ⇨ $\dfrac{\partial^2 \Delta g_m}{\partial x^2} > 0$

Free Energy Change due to Mixing (for Wilson Equation)

$$\frac{\Delta g_m}{RT} = \frac{g^E}{RT} + x_1 \ln x_1 + x_2 \ln x_2 ,\ldots \frac{g^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12} x_2) - x_2 \ln(\Lambda_{21} x_1 + x_2)$$

$$\frac{\partial}{\partial x_1}\left(\frac{\Delta g_m}{RT}\right) = -\ln(x_1 + \Lambda_{12}x_2) - x_1 \frac{1-\Lambda_{12}}{x_1 + \Lambda_{12}x_2} + \ln(\Lambda_{21}x_1 + x_2) - x_2 \frac{\Lambda_{21} - 1}{\Lambda_{21}x_1 + x_2} + \ln x_1 + 1 - \ln x_2 - 1$$

$$\frac{\partial^2}{\partial x_1^2}\left(\frac{\Delta g_m}{RT}\right) = -\frac{1-\Lambda_{12}}{x_1+\Lambda_{12}x_2} - \frac{1-\Lambda_{12}}{x_1+\Lambda_{12}x_2} + x_1\left(\frac{1-\Lambda_{12}}{x_1+\Lambda_{12}x_2}\right)^2 + \frac{\Lambda_{21}-1}{\Lambda_{21}x_1+x_2} + \frac{\Lambda_{21}-1}{\Lambda_{21}x_1+x_2} + x_2\left(\frac{\Lambda_{21}-1}{\Lambda_{21}x_1+x_2}\right)^2 + \frac{1}{x_1} + \frac{1}{x_2}$$

$$= -\frac{2(1-\Lambda_{12})}{x_1+\Lambda_{12}x_2} + x_1\left(\frac{1-\Lambda_{12}}{x_1+\Lambda_{12}x_2}\right)^2 + \frac{1}{x_1} + \frac{2(\Lambda_{21}-1)}{\Lambda_{21}x_1+x_2} + x_2\left(\frac{\Lambda_{21}-1}{\Lambda_{21}x_1+x_2}\right)^2 + \frac{1}{x_2}$$

$$= \frac{1}{x_1(x_1+\Lambda_{12}x_2)^2}\left[-2x_1(1-\Lambda_{12})(x_1+\Lambda_{12}x_2) + x_1^2(1-\Lambda_{12})^2 + (x_1+\Lambda_{12}x_2)^2\right]$$

$$+ \frac{1}{x_2(\Lambda_{21}x_1+x_2)^2}\left[2x_2(\Lambda_{21}-1)(\Lambda_{21}x_1+x_2) + x_2^2(\Lambda_{21}-1)^2 + (\Lambda_{21}x_1+x_2)^2\right]$$

$$= \frac{1}{x_1(x_1+\Lambda_{12}x_2)^2}\left[-2x_1(x_1+\Lambda_{12}x_2-\Lambda_{12}x_1-\Lambda_{12}^2x_2) + x_1^2(1-2\Lambda_{12}+\Lambda_{12}^2) + (x_1^2+2\Lambda_{12}x_1x_2+\Lambda_{12}^2x_2^2)\right]$$

$$+ \frac{1}{x_2(\Lambda_{21}x_1+x_2)^2}\left[2x_2(\Lambda_{21}^2x_1+\Lambda_{21}x_2-\Lambda_{21}x_1-x_2) + x_2^2(\Lambda_{21}^2-2\Lambda_{21}+1) + (\Lambda_{21}^2x_1^2+2\Lambda_{21}x_1x_2+x_2^2)\right]$$

$$= \frac{1}{x_1(x_1+\Lambda_{12}x_2)^2}\left[-2x_1^2 - 2x_1\Lambda_{12}x_2 + 2\Lambda_{12}x_1^2 + 2\Lambda_{12}^2x_1x_2 + x_1^2 - 2\Lambda_{12}x_1^2 + \Lambda_{12}^2x_1^2 + x_1^2 + 2\Lambda_{12}x_1x_2 + \Lambda_{12}^2x_2^2\right]$$

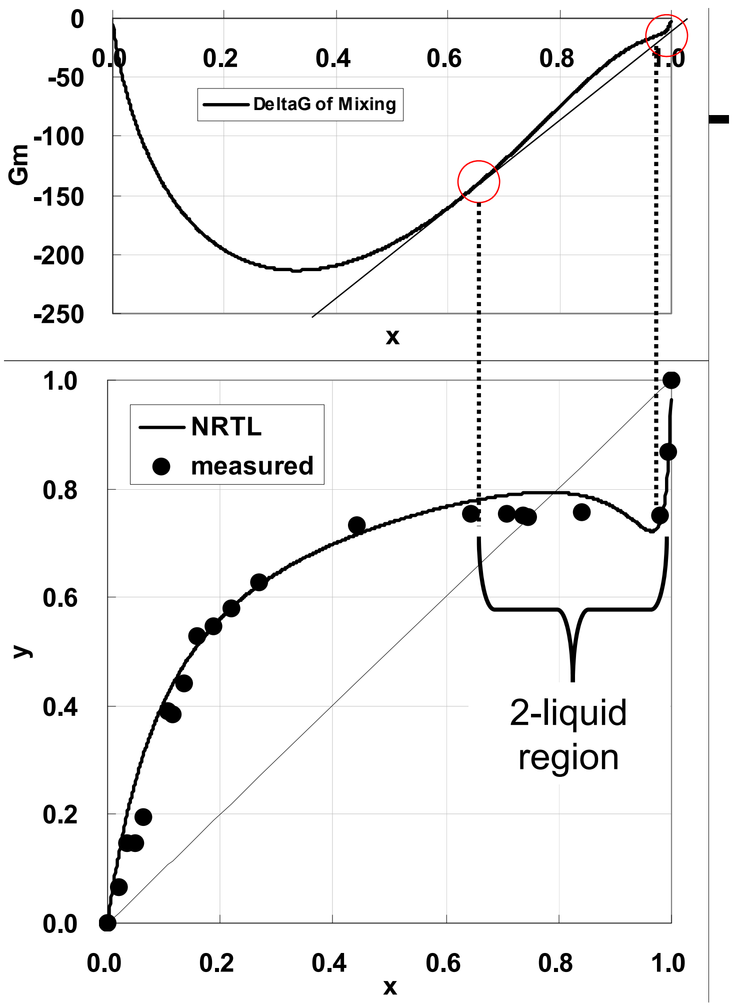
$$+ \frac{1}{x_2(\Lambda_{21}x_1+x_2)^2}\left[2\Lambda_{21}^2x_1x_2 + 2\Lambda_{21}x_2^2 - 2\Lambda_{21}x_1x_2 - 2x_2^2 + \Lambda_{21}^2x_2^2 - 2\Lambda_{21}x_2^2 + x_2^2 + \Lambda_{21}^2x_1^2 + 2\Lambda_{21}x_1x_2 + x_2^2\right]$$

$$= \frac{1}{x_1(x_1+\Lambda_{12}x_2)^2}\left[2\Lambda_{12}^2x_1x_2 + \Lambda_{12}^2x_1^2 + \Lambda_{12}^2x_2^2\right] + \frac{1}{x_2(\Lambda_{21}x_1+x_2)^2}\left[2\Lambda_{21}^2x_1x_2 + \Lambda_{21}^2x_2^2 + \Lambda_{21}^2x_1^2\right]$$

$$= \frac{\Lambda_{12}^2(x_1+x_2)^2}{x_1(x_1+\Lambda_{12}x_2)^2} + \frac{\Lambda_{21}^2(x_1+x_2)^2}{x_2(\Lambda_{21}x_1+x_2)^2} = \frac{\Lambda_{12}^2}{x_1(x_1+\Lambda_{12}x_2)^2} + \frac{\Lambda_{21}^2}{x_2(\Lambda_{21}x_1+x_2)^2} > 0$$

In the Wilson equation, the second-order derivative of the free energy curve of mixing is > 0 no matter what the parameter values are, so it cannot represent liquid-liquid equilibrium.

Solutic

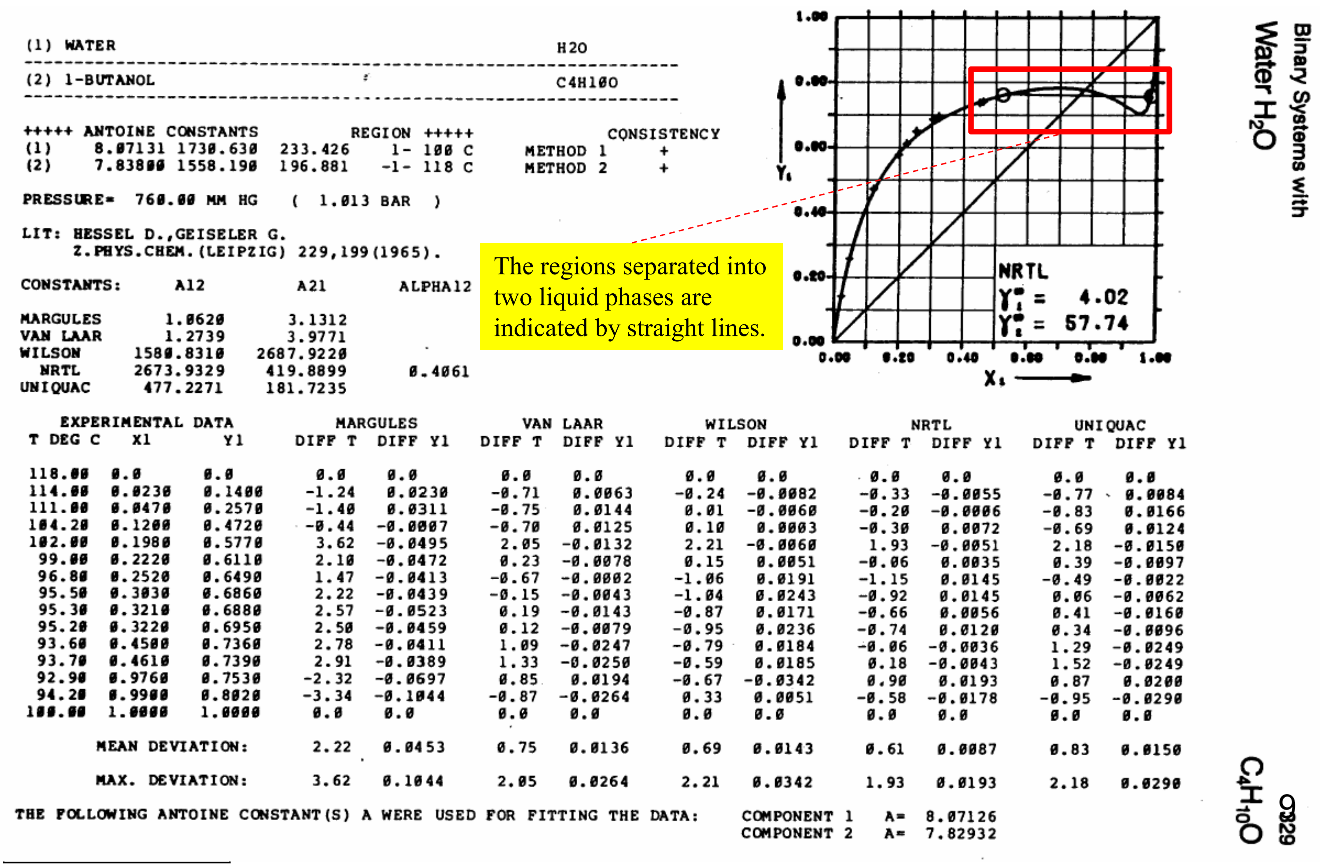


Determination of two liquid phase regions from mixed free energy change (water - n-butanol vapor-liquid equilibrium)

From the tangent to the free energy change curve of mixing, it can be seen that there are two liquid phases in the region of x1 = 0.65 - 0.95.

The range of liquid-liquid phase separation given by DECHEMA data on the next page is almost the same.

Water - n-Butanol Vapor Liquid Equilibrium
(DECHEMA Chem. Data Series)



(1) WATER H2O

(2) 1-BUTANOL C4H10O

+++++ ANTOINE CONSTANTS REGION +++++

				REGION
(1)	8.07131	1730.630	233.426	1- 100 C
(2)	7.83800	1558.190	196.881	-1- 118 C

CONSISTENCY
METHOD 1 +
METHOD 2 +

PRESSURE= 760.00 MM HG (1.013 BAR)

LIT: HESSEL D.,GEISELER G.
Z.PHYS.CHEM.(LEIPZIG) 229,199(1965).

CONSTANTS:	A12	A21	ALPHA12
MARGULES	1.0620	3.1312	
VAN LAAR	1.2739	3.9771	
WILSON	1580.8310	2687.9220	
NRTL	2673.9329	419.8899	0.4061
UNIQUAC	477.2271	181.7235	

EXPERIMENTAL DATA			MARGULES		VAN LAAR		WILSON		NRTL		UNIQUAC	
T DEG C	X1	Y1	DIFF T	DIFF Y1	DIFF T	DIFF Y1	DIFF T	DIFF Y1	DIFF T	DIFF Y1	DIFF T	DIFF Y1
118.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
114.00	0.0230	0.1400	-1.24	0.0230	-0.71	0.0063	-0.24	-0.0082	-0.33	-0.0055	-0.77	0.0084
111.00	0.0470	0.2570	-1.40	0.0311	-0.75	0.0144	0.01	-0.0060	-0.20	-0.0006	-0.83	0.0166
104.20	0.1200	0.4720	-0.44	-0.0007	-0.70	0.0125	0.10	0.0003	-0.30	0.0072	-0.69	0.0124
102.00	0.1980	0.5770	3.62	-0.0495	2.05	-0.0132	2.21	-0.0060	1.93	-0.0051	2.18	-0.0150
99.00	0.2220	0.6110	2.10	-0.0472	0.23	-0.0078	0.15	0.0051	-0.06	0.0035	0.39	-0.0097
96.80	0.2520	0.6490	1.47	-0.0413	-0.67	-0.0002	-1.06	0.0191	-1.15	0.0145	-0.49	-0.0022
95.50	0.3030	0.6860	2.22	-0.0439	-0.15	-0.0043	-1.04	0.0243	-0.92	0.0145	0.06	-0.0062
95.30	0.3210	0.6880	2.57	-0.0523	0.19	-0.0143	-0.87	0.0171	-0.66	0.0056	0.41	-0.0160
95.20	0.3220	0.6950	2.50	-0.0459	0.12	-0.0079	-0.95	0.0236	-0.74	0.0120	0.34	-0.0096
93.60	0.4500	0.7360	2.78	-0.0411	1.09	-0.0247	-0.79	0.0184	-0.06	-0.0036	1.29	-0.0249
93.70	0.4610	0.7390	2.91	-0.0389	1.33	-0.0250	-0.59	0.0185	0.18	-0.0043	1.52	-0.0249
92.90	0.9760	0.7530	-2.32	-0.0697	0.85	0.0194	-0.67	-0.0342	0.90	0.0193	0.87	0.0200
94.20	0.9900	0.8020	-3.34	-0.1044	-0.87	-0.0264	0.33	0.0051	-0.58	-0.0178	-0.95	-0.0290
100.00	1.0000	1.0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
MEAN DEVIATION:			2.22	0.0453	0.75	0.0136	0.69	0.0143	0.61	0.0087	0.83	0.0150
MAX. DEVIATION:			3.62	0.1044	2.05	0.0264	2.21	0.0342	1.93	0.0193	2.18	0.0290

THE FOLLOWING ANTOINE CONSTANT(S) A WERE USED FOR FITTING THE DATA: COMPONENT 1 A= 8.07126
COMPONENT 2 A= 7.82932

Binary Systems with
Water H_2O

$C_4H_{10}O$

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The regions separated into two liquid phases are indicated by straight lines.

Estimation of Vapor-Liquid Equilibrium from Liquid-Liquid Equilibrium

Example where the NRTL Equation can be applied to both Vapor-Liquid Equilibrium and Liquid-Liquid Equilibrium

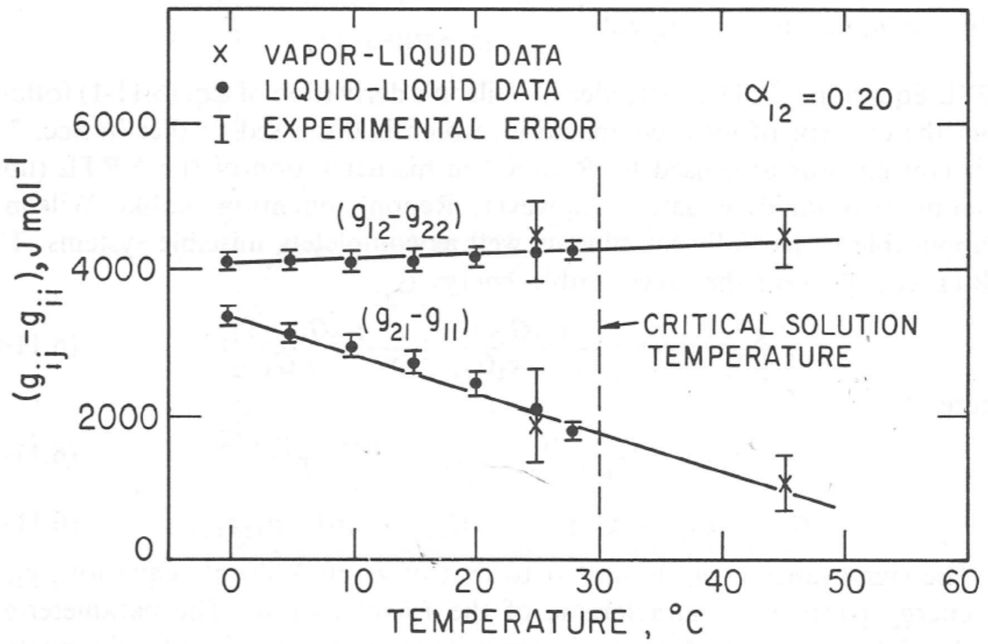


Figure 6-17 Parameters in NRTL equation for the nitroethane(1)/iso-octane(2) system calculated from vapor-liquid and liquid-liquid equilibrium data.

The figure on the left shows that the parameters obtained from liquid-liquid equilibrium data at 30˚C or below and the vapor-liquid equilibrium parameters obtained at 25˚C and 45˚C are collinear.

In other words, it shows that high-temperature vapor-liquid equilibrium can be estimated using the NRTL equation if low temperature liquid-liquid equilibrium data is available.

"Molecular Thermodynamics of Fluid-Phase Equilibria (Second edition) "
(Prausnitz, J. M et al., Prentice-Hall p238)

Estimation of Vapor-Liquid Equilibrium from Liquid-Liquid Equilibrium Data

Using the fact that the NRTL equation can be applied to both vapor-liquid equilibrium and liquid-liquid equilibrium, the NRTL parameters τ_{ij} are obtained from the water - n-butanol mutual solubility data at each temperature and correlated with $1/T$. It is assumed that $\alpha = 0.4427$.

Basic Liquid-Liquid Equilibrium Equation

$$f_i^{L1} = f_i^{L2} \; : \; \gamma_i^{L1} x_i^{L1} = \gamma_i^{L2} x_i^{L2}$$

NRTL Equation

$$\ln\gamma_1 = x_2^2\left[\frac{\tau_{21}G_{21}^2}{(x_1 + x_2G_{21})^2} + \frac{\tau_{12}G_{12}}{(x_1G_{12} + x_2)^2}\right]$$

$$\ln\gamma_2 = x_1^2\left[\frac{\tau_{12}G_{12}^2}{(x_2 + x_1G_{12})^2} + \frac{\tau_{21}G_{21}}{(x_2G_{21} + x_1)^2}\right]$$

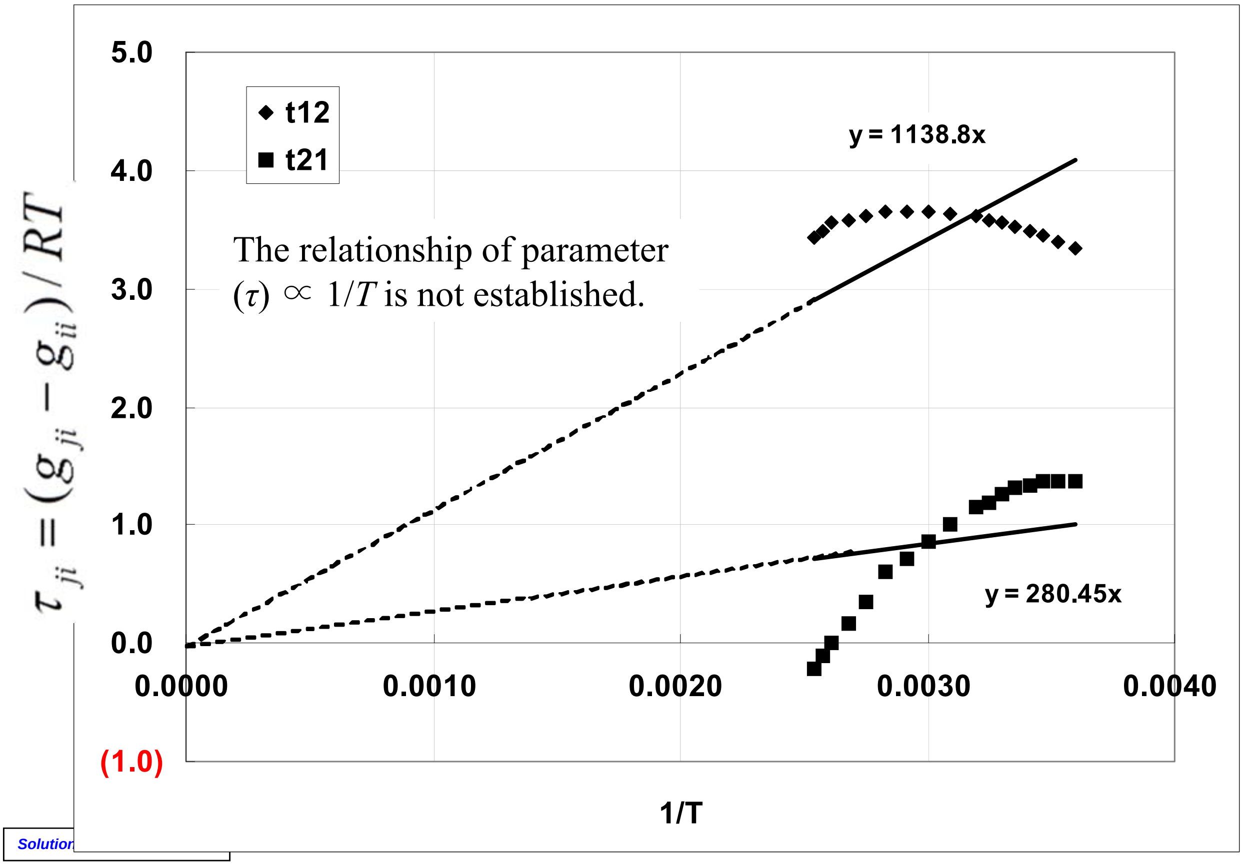
$$\tau_{ji} = (g_{ji} - g_{ii})/RT$$

$$G_{ji} = \exp(-\alpha\tau_{ji})$$

LLE measurement		
temp	x1'	x1"
5	0.5016	0.9750
10	0.5019	0.9768
15	0.5049	0.9787
20	0.5082	0.9798
25	0.5113	0.9811
30	0.5166	0.9818
35	0.5233	0.9825
40	0.5285	0.9831
50	0.5432	0.9835
60	0.5601	0.9833
70	0.5811	0.9828
80	0.5970	0.9823
90	0.6392	0.9796
100	0.6775	0.9760
110	0.7126	0.9723
115	0.7409	0.9656
120	0.7780	0.9554
125.15	0.8952	0.8952

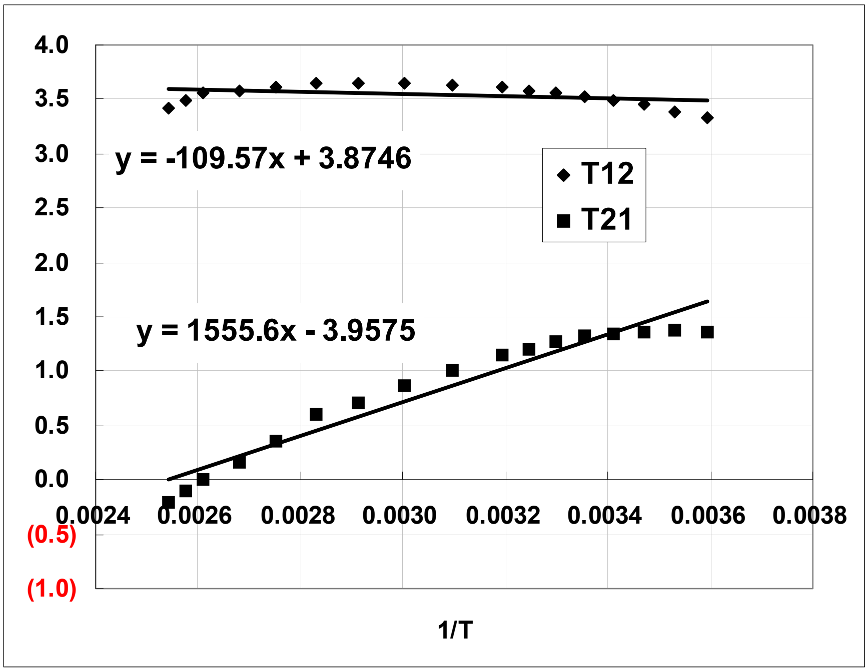
"Process Sekkei no tameno Souheikou"
(in Japanese)

Temperature Dependence of NRTL Parameters (Wide Temperature Range)



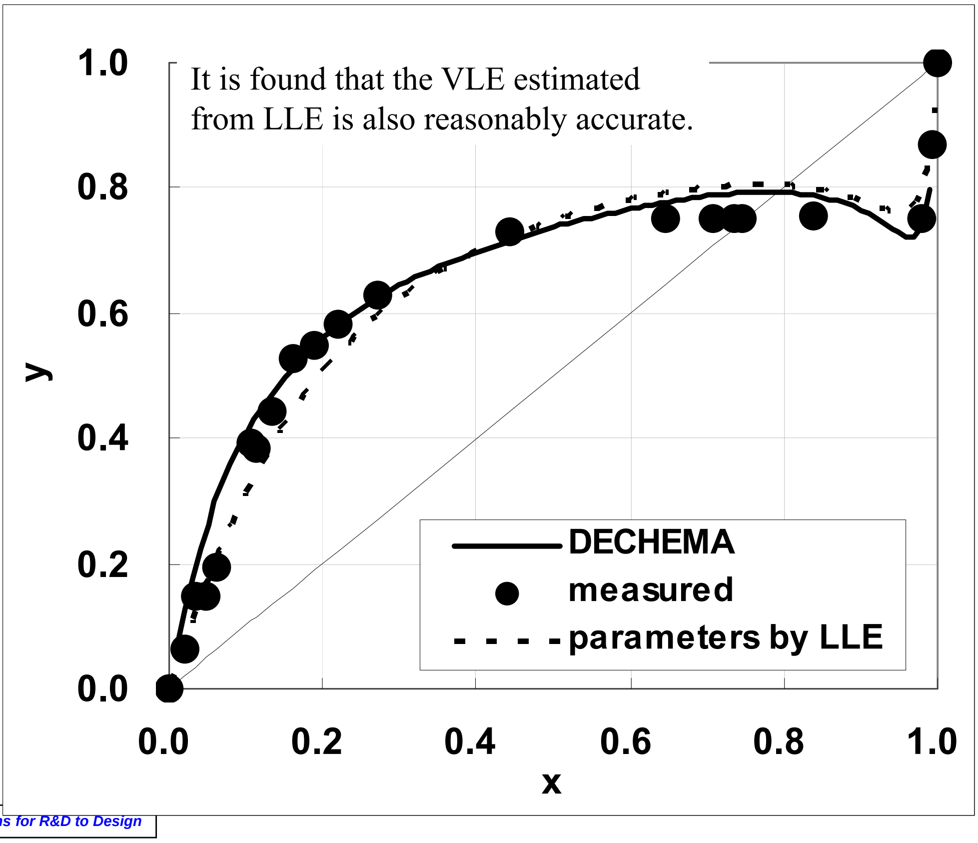
The relationship of parameter (τ) $\propto$ $1/T$ is not established.

Temperature Dependence of NRTL Parameters (Narrow Temperature Range)



It can be seen that the temperature dependence of the parameters obtained from the liquid-liquid equilibrium data has some degree of linearity in a narrow temperature range.

We will perform the vapor-liquid equilibrium calculation from the straight line approximation section.

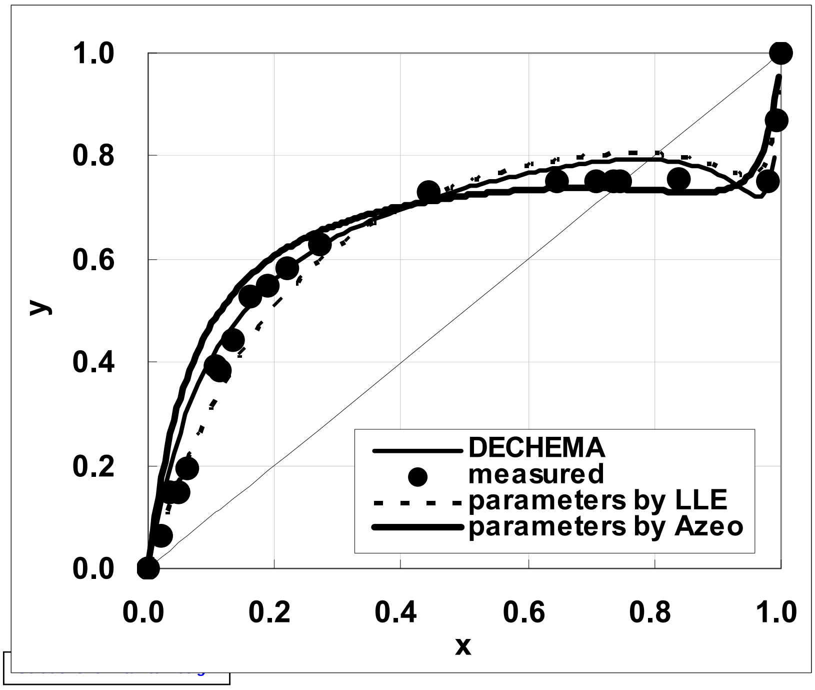


It is found that the VLE estimated from LLE is also reasonably accurate.

Comparison with Vapor-Liquid Equilibrium Estimation from Azeotropic Data

Vapor-liquid equilibrium parameters are determined from water - n-butanol azeotropic data and a vapor-liquid equilibrium calculation is performed.

Azeotropic point
P=760
t=92.7
x1=0.737



The estimation accuracy is slightly higher with the calculation from azeotropic data, but both can be considered to have sufficient accuracy to conduct preliminary studies.

Conclusion

A vapor-liquid equilibrium calculation was carried out by linearly extrapolating the parameters obtained from liquid-liquid equilibrium data using the NRTL equation that is applicable to both vapor-liquid equilibrium and liquid-liquid equilibrium.
As a result, it was found that this method is sufficiently accurate for a preliminary separation study although it is somewhat inferior to the estimation from azeotropic data.