

Determination of Vapor-Liquid Equilibrium Parameters Using Azeotropic Data



September 1, 2011

PreFEED Corporation

Hiromasa Taguchi

Introduction

- The vapor-liquid equilibrium calculations using activity coefficient models such as the Wilson and NRTL models are widely practiced and have a number of successful applications.
- Binary parameters are required in order to use activity coefficient models, and they are generally determined from actually measured vapor-liquid equilibrium data.
- On the other hand, even when vapor-liquid equilibrium data is not measured, it is possible to estimate vapor-liquid equilibrium with relatively high accuracy when azeotropic data can be used.
- Here we will consider a method for estimating the binary parameters of an activity coefficient model using azeotropic data, and examine the accuracy of this method.

- To verify the estimation accuracy of azeotropic data, the following systems will be examined.

	Component 1	Component 2	Condition	Azeotropic type
1	Ethanol	Water	Constant Pressure	Minimum Boiling Azeotrope
2	Methanol	Benzene	Constant Temperature	Minimum Boiling Azeotrope
3	Acetone	Chloroform	Constant Pressure	Maximum Boiling Azeotrope

- The Wilson equation is applied as the activity coefficient model.

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right)$$

$$\ln \gamma_2 = -\ln(\Lambda_{21}x_1 + x_2) - x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right)$$

Determination of Vapor-Liquid Equilibrium Parameters from Azeotropic Data

$$Py_1 = \gamma_1 x_1 P_1^o$$

$$Py_2 = \gamma_2 x_2 P_2^o$$

$$\gamma_1 = \frac{Py_1}{x_1 P_1^o}$$

$$\gamma_2 = \frac{Py_2}{x_2 P_2^o}$$

At the azeotropic point, since the vapor and liquid compositions are the same, the activity coefficients are determined by the total pressure and vapor pressure. In this case, when an azeotropic composition is given, parameters of the activity coefficient equation can be determined.

$$x_i = y_i \dots \text{at.. azeotrope}$$

$$\therefore \gamma_1 = \frac{P}{P_1^o}, \gamma_2 = \frac{P}{P_2^o}$$

Flow of calculation: (for Wilson equation)

- Input azeotropic data

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right)$$

$$\ln \gamma_2 = -\ln(\Lambda_{21}x_1 + x_2) - x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right)$$

→ Determine Λ → Calculate VLE in the entire composition range

EQUATRAN Source text

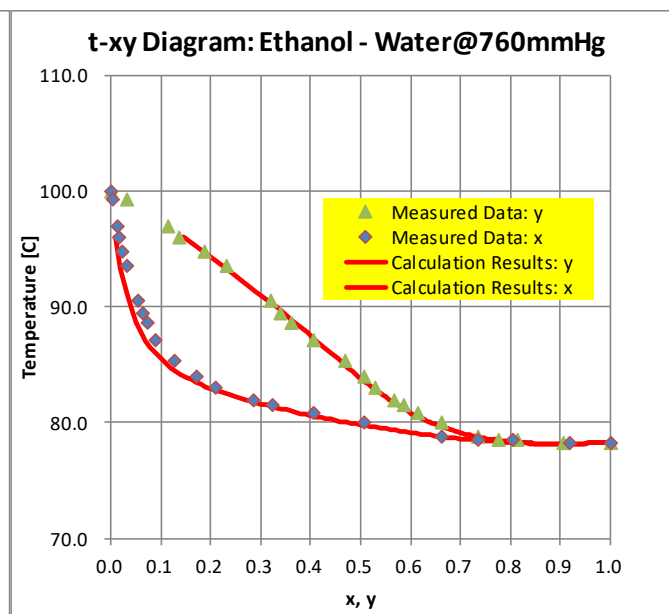
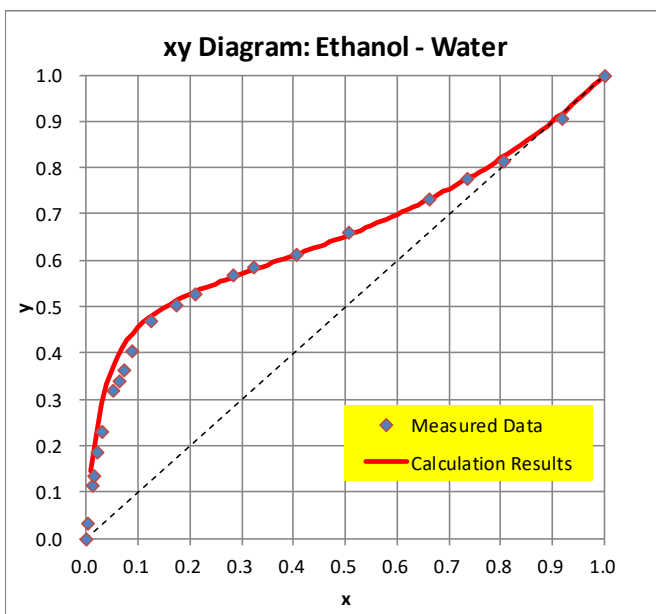
```
// Ethanol-Water by azeotropic data
P*y1=g1*x1*P10
P*y2=g2*x2*P20
x1+x2=1
y1+y2=1
log(g1)=-log(x1+L12*x2)+x2*(L12/(x1+L12*x2)-L21/(L21*x1+x2))
log(g2)=-log(L21*x1+x2)-x1*(L12/(x1+L12*x2)-L21/(L21*x1+x2))
log10(P10)=8.21337-1652.05/(t+231.48) // Ethanol
log10(P20)=7.94916-1657.46/(t+227.02) // Water

// Azeotropic Data
x1=0.8941
y1=0.8941
t=78.15
P=760

Output L12, L21
```

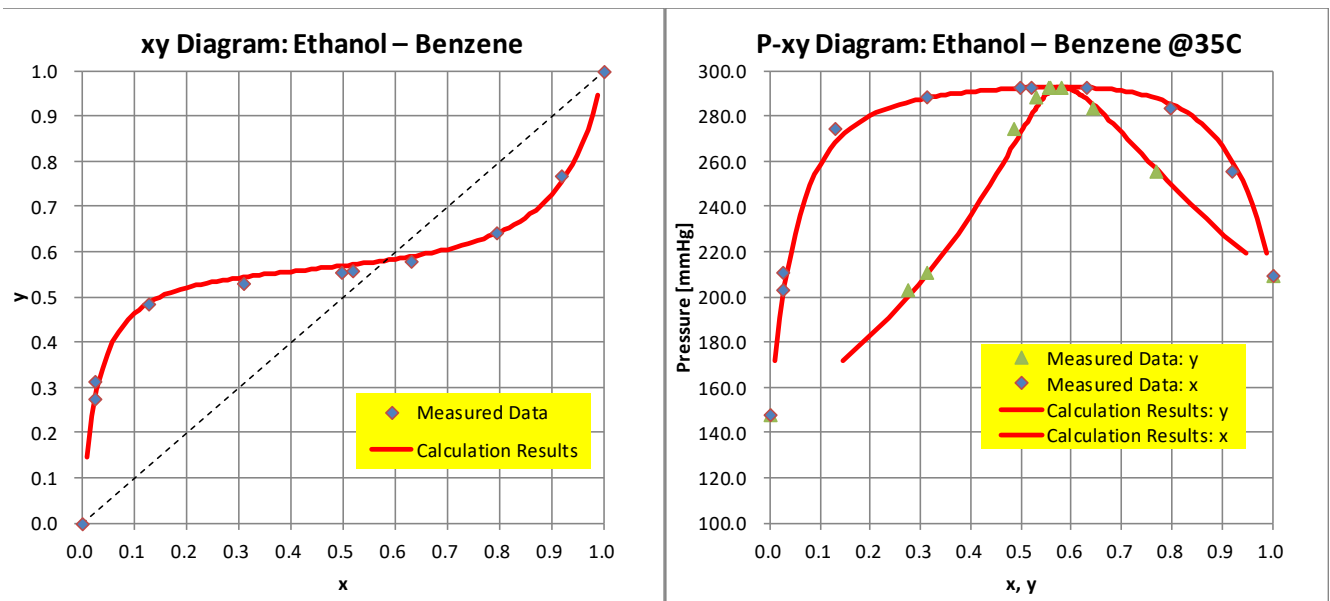
Wilson Eq.

Azeotropic Data



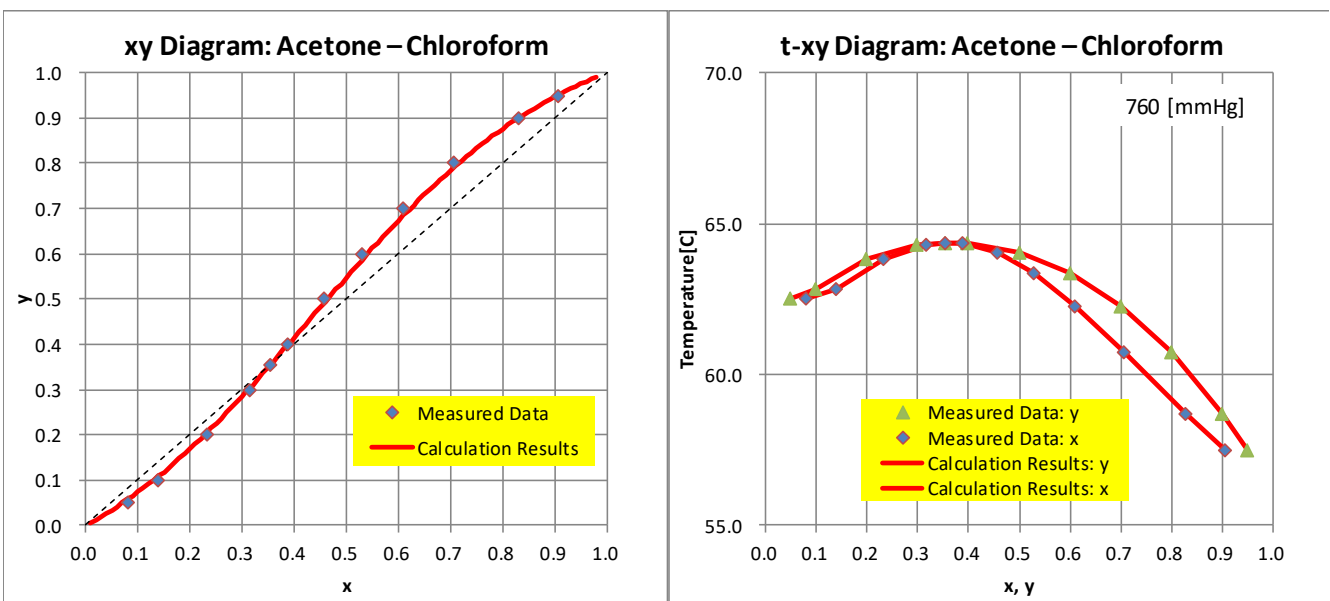
```
<< results >>
L12      = 0.1283514
L21      = 0.9177398
```

Results 2: Ethanol - Benzene (t=35C)



```
<< results >>
L12      = 0.1527515
L21      = 0.2861521
```

Results 3: Acetone - Chloroform (P=760 mmHg)



Although only azeotropic data is used, it can be seen that the VLE can be represented with high accuracy.

```
<< results >>
L12      = 1.30312
L21      = 1.401835
```

Flow of calculation: (for Wilson equation)

- Input azeotropic data

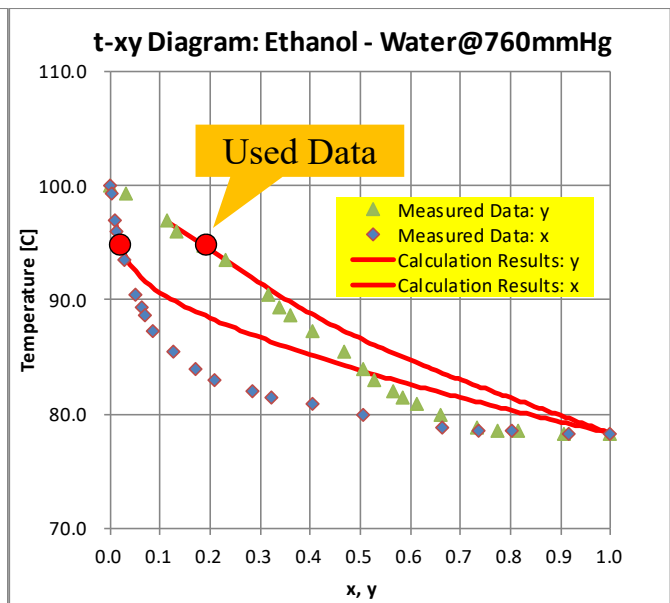
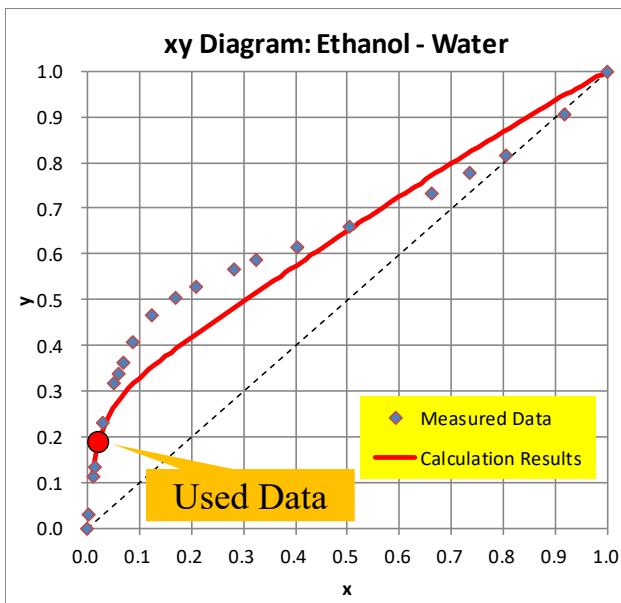
$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right)$$

$$\ln \gamma_2 = -\ln(\Lambda_{21}x_1 + x_2) - x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right)$$

→ Determine Λ → Calculate VLE in the entire composition range

It is possible to obtain the above algebraic equation even if data other than the azeotropic point is used.
Let us examine what kind of results will be obtained.

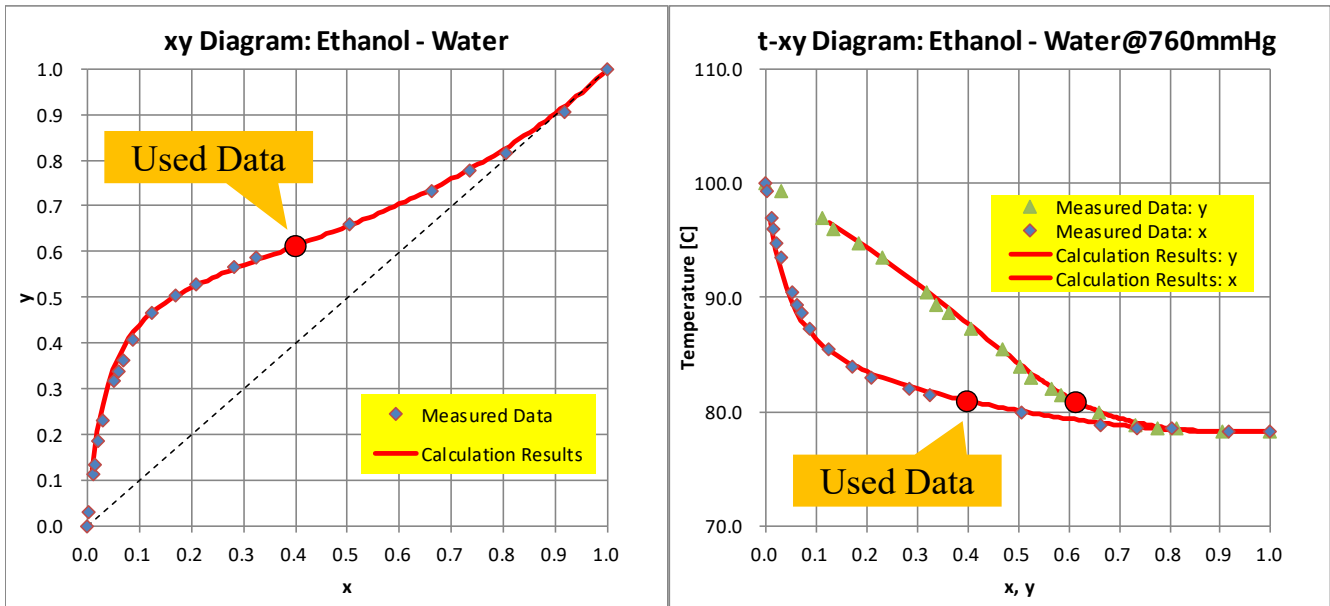
Results: 4. Ethanol - Water (Data other than Azeotrope)



Used Data:

x	y	t	P
0.0220	0.1860	94.8	760

```
<<  results  >>
L12      =  0.06029955
L21      =  1.797075
```



Used Data:

x	y	t	P
0.4050	0.6140	80.9	760

Solutions for R&D to Design

```
<<  results  >>
L12      =  0.15321
L21      =  0.9305851
```

11

Conclusion

- Binary parameters were estimated using only azeotropic data for a minimum boiling azeotropic mixture under constant pressure or constant temperature conditions and for a maximum boiling azeotropic mixture under constant pressure conditions.
- When compared with measured values, it was found that estimations can be made with a high accuracy in all three cases. In general, an estimation using azeotropic data is highly accurate.
- Estimations are possible using data other than the azeotropic point. Depending on the data used, in some cases the errors are large, and in other cases estimations can be made with a high accuracy.