Measurement of Isobaric Vapor-Liquid Equilibria for Binary Systems Containing Tetrahydrofuran Using a Simple and Automatic Apparatus

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Tetrahydrofuran (THF) is an organic raw material, a precursor of polymers, and a solvent of polymer such as polystyrene, poly (methyl methacrylate), polycarbonate, and cleaning solvent of semiconductor.

An efficient separation and recycle of THF from aqueous waste streams is an important concept in the chemical industries, even considering from viewpoint of environmental and resource issues.
THF and water form minimum boiling azeotrope containing 20 mol% water at atmospheric pressure.

Separating solvent of THF+water system using azeotropic distillation

\textit{n-pentane}


The measurement of VLE data are important for discussing the effect of another alkanes.
The objectives of this presentation are:

(1) To propose a simple and automatic apparatus of measuring VLE data.

(2) To measure the bubble point data at reduced pressures for THF+ water and THF + three n-alkanes (pentane, hexane and heptane) using a simple and automatic apparatus.

(3) To determine the NRTL parameters using the bubble point data.
Apparatus

Fig. 1  Schematic diagram of simple and automatic apparatus for measuring vapor-liquid equilibria (Japan Patent No. 4143954 (2008))
Features of Apparatus

/ Application of PTx method that does not need analysis of composition

/ Application of automatic operation of some items that needs the skill of experimenter.

a. Adjustment of heat to flask
b. Adjustment of pressures in equipment
c. Transmission of experimental data to PC computer
Fig.2 Flow chart used for measuring bubble point

- **Start** → **Reset**
- **Pressure Control**
  - **Pressure Control (Low)**
  - **Pressure Control (High)**
  - **Pressure Control (Midle)**
- **Resistance Value of Pt Sensor** → **Convert to Temperature**
- **Resistance Value of Pressure Sensor** → **Convert to Pressure**
- **Display Temperature and Pressure**
- **Calculation of Temperature** ($T_{ave}, T_{max}, T_{min}$)
- **20 Counts?**
  - **No**
  - **Yes**
    - **Abs[$T_{max}(Sample) - T_{min}(Sample)$] < 0.3**
    - **Abs[$T_{max}(Water) - T_{min}(Water)$] < 0.3**
    - **Abs[$T_{ave}(Water) - T_{obj}(Water)$] < 0.05**
- **Equilibrium Temperature**
Fig. 3 Pressure-Control System

Buffer tank

To the system

Actual Pressure P

Valve

High Pressure P+\alpha

Valve

Low Pressure P-\alpha

Valve

VACUUM PUMP

Valve

(1)\sim(6): Electromagnetic valves

* Valves (1) to (4) are controled using P-control.

* Valves (5) to (6) are controled using PID-control.

* The values of $\alpha$ change according to objective pressure.
Fig. 4(a) Experimental results of bubble points for the THF(1)+Water(2) at 40.00-101.3kPa
Fig. 4(b) Experimental results of bubble points for THF + n-pentane system at 40.00-101.3kPa
Fig. 4(c) Experimental results of bubble points at 40.00-101.3kPa
Fig. 5 Bubble points for THF(1)+n-alkanes(2) system (101 kPa)
NRTL equation (Renon and Prausnitz, 1968)

\[
\ln \gamma_i = x_j^2 \left[ \tau_{ji} \left( \frac{G_{ji}}{x_i + x_j G_{ji}} \right)^2 + \frac{\tau_{ij} G_{ij}}{(x_j + x_i G_{ij})^2} \right]
\]

\(G_{ij} = \exp(-\alpha_{12} \tau_{ij})\) \hspace{1cm} (3)
\(\tau_{ij} = (g_{ij} - g_{jj})/RT\) \hspace{1cm} (4)

Objective function

\[
F_{obj} = \sum_{k=1}^{NDP} \left( T_{exp} - T_{cal} \right)_k^2
\]

\(\alpha_{12} : \) Non randomness parameter
\(g_{ij}-g_{jj} : \) Binary interaction parameters

NDP : Number of Data Point
**Correlated results (binary system)**

Table 1 Correlated results of bubble points for the THF(1)+Water(2) using NRTL equation

<table>
<thead>
<tr>
<th>P/kPa</th>
<th>$g_{12}-g_{22}$/J·mol$^{-1}$</th>
<th>$g_{21}-g_{11}$/J·mol$^{-1}$</th>
<th>$\alpha_{12}$</th>
<th>$\Delta T$/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>40.0</td>
<td>4285.24</td>
<td>6261.05</td>
<td>0.448</td>
<td>0.1</td>
</tr>
<tr>
<td>53.3</td>
<td>4267.69</td>
<td>6246.48</td>
<td>0.450</td>
<td>0.1</td>
</tr>
<tr>
<td>66.7</td>
<td>4252.84</td>
<td>6434.69</td>
<td>0.448</td>
<td>0.1</td>
</tr>
<tr>
<td>80.0</td>
<td>4238.18</td>
<td>6800.83</td>
<td>0.448</td>
<td>0.1</td>
</tr>
<tr>
<td>93.3</td>
<td>4292.10</td>
<td>6940.96</td>
<td>0.452</td>
<td>0.1</td>
</tr>
<tr>
<td>101</td>
<td>4369.14</td>
<td>6961.42</td>
<td>0.452</td>
<td>0.1</td>
</tr>
</tbody>
</table>
### Correlated results (binary system)

Table 2 Correlated results of vapor-liquid equilibrium for the THF(1)+solvent(2) using NRTL equation

| system                  | Parameter               | $|\Delta T|_{av}$ [K] | $|\Delta T|_{max}$ [K] |
|-------------------------|-------------------------|---------------------|---------------------|
| THF(1)+water(2)         | $g_{12}-g_{22}=4224.74$ [J/mol] | 0.2                 | 1.7                 |
|                         | $g_{21}-g_{11}=6582.13$ [J/mol] |                     |                     |
|                         | $\alpha_{12}=0.446$ [-] |                     |                     |
| THF(1)+n-Pentane(2)     | $g_{12}-g_{22}=-76.292$ [J/mol] | 0.2                 | 0.7                 |
|                         | $g_{21}-g_{11}=1846.24$ [J/mol] |                     |                     |
|                         | $\alpha_{12}=0.300$ [-] |                     |                     |
| THF(1)+n-Hexane(2)      | $g_{12}-g_{22}=1540.52$ [J/mol] | 0.1                 | 0.6                 |
|                         | $g_{21}-g_{11}=125.802$ [J/mol] |                     |                     |
|                         | $\alpha_{12}=0.300$ [-] |                     |                     |
| THF(1)+n-Heptane(2)     | $g_{12}-g_{22}=3246.34$ [J/mol] | 0.1                 | 0.8                 |
|                         | $g_{21}-g_{11}=-1296.9$ [J/mol] |                     |                     |
|                         | $\alpha_{12}=0.300$ [-] |                     |                     |
Correlated results (binary system)

Fig. 6(a) Correlated results of vapor-liquid equilibrium at for THF(1)+water(2) system 40.00-101.3kPa using NRTL equation

a1) Each pressure

a2) Total experimental data
Fig. 6(a) Correlated results of vapor-liquid equilibrium at 40.00-101.3kPa using NRTL equation

(a) THF(1)+Water(2)

(b) THF(1)+n-Pentane(2)
Correlated results (binary system)

c) THF(1) + n-Hexane(2)

d) THF(1) + n-Heptane(2)

Fig. 6(b) Correlated results of vapor-liquid equilibrium at 40.00-101.3 kPa using NRTL equation
Conclusions

(1) A simple and automatic apparatus of measuring VLE data is proposed in order to measure VLE data rapidly.

(2) The bubble points for four systems containing tetrahydrofuran have been measured at reduced pressures using the simple and automatic apparatus.

(3) The NRTL parameters have been determined using the experimental bubble points.

(4) The determined NRTL parameters will be useful for discussing the azeotropic distillation process.