Expt. MT 302

Differential Distillation

Aim
To verify the Rayleigh’s equation for a differential distillation in a binary system.

Theory
In the case of a differential distillation, the vapour at any time is in equilibrium with the liquid from which it rises but changes continuously in the composition. Thus, the mathematical approach used must be differential. Assume that \( L \) mol of liquid in the still of composition \( x \) mol fraction \( A \) and that an amount \( dD \) mol of distillate is vaporized, of mol fraction \( y^* \) in equilibrium with the liquid.

Material Balance
The rate of depletion of liquid is equal to the rate of distillate output. The instantaneous rate of depletion of a component in the liquid is therefore, \( \text{In - out} = \text{accumulation} \)

\[
0 - dD = dL
\]  
(1)

Taking balance on more volatile component,

\[
0 - y^*dD = d(Lx)
\]  
(2)

\[
0 - y^*dD = xdL + Ldx
\]  
(3)

\[
y^*dL = xdL + Ldx
\]  
(4)

Therefore rearrangement gives,

\[
\int_{W}^{F} \frac{dL}{L} = \int_{xw}^{xF} \frac{dx}{y^* - x}
\]  
(5)

This equation can be integrated to get the following form which is called the Rayleigh’s Equation,

\[
\ln \frac{F}{W} = \int_{xw}^{xF} \frac{dx}{y^* - x}
\]  
(6)
where, \( F \) = moles of feed of composition \( x_F \), \( W \) = moles of residual liquid of composition \( x_W \), \( W \) and \( x_w \) can be obtained by material balance,

\[
F = D + W \tag{7}
\]

\[
F x_F = D x_D + W x_W \tag{8}
\]

The integral in eqn. [5] can be solved analytically (provided the relationship between \( y^* \) and \( x \) is available) or graphically (calculating the area under the curve for the plot of \( 1/(y^* - x) \) vs \( x \).
Apparatus

![Schematic of the setup](image)

**Figure MT 302.0.1: Schematic of the setup**

**Procedure**

1. Prepare a calibration plot of mole fraction ($x$) vs. refractive index ($\eta$) of pure components $A$ and $B$.

2. Weigh 8 nos. of tagged stoppered conical flasks.

3. Start the flow of water through the condenser.

4. Fill $\frac{3}{4}$th (approx. 300 ml) volume of the distillation flask with a mixture of $A$ and $B$ of known composition ($x_F$). The mixture is weighed ($w$) before charging in the distillation flask.

5. Start heating at a slow rate. When the mixture starts boiling, collect the distillate in a weighed 50 ml flask. After approximately 30 ml of the distillate has been collected, remove the flask and collect next 8 to 10 drops of the distillate in tagged test-tube and then put another flask for the collection of the distillate. This procedure should be repeated for collecting 8 distillate samples.

6. Measure the refractive indices (RI) of the samples collected in the test-tubes ($\eta_{1t}, \eta_{2t},...,\eta_{12t}$). Weigh the samples collected in the conical flasks ($w_1, w_2,..., w_{12}$). Measure the RI of the bulk from each of the flasks ($\text{eta}_{1b}, \text{eta}_{2b},..., \eta_{12b}$).

**Observations and Calculations**

**Data from the literature**

1. Molecular weights of $A$ and $B$.

2. Refractive indices of $A$ and $B$.

3. Densities of $A$ and $B$.

4. Vapour liquid equilibrium data for $A$ and $B$ at atmospheric pressure.
Calibration data for mole fraction vs. RI

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<thead>
<tr>
<th>S.N.</th>
<th>Mole fraction of $A$</th>
<th>RI</th>
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Calculations

1. Calculate $D$ (amount of distillate) (from weighed 30 ml sample) and $x_D$ (distillate composition) (from refractive index of 30 ml sample) for each sample.

2. Calculate $W$ (amount of residue still left in the flask) and $x_W$ (composition of residue) using Eqn. 7 and 8 for each fraction.

3. Calculate $y^*$ (vapor phase composition) for each sample (from Refractive index of 8 drops collected.)

4. Calculate $x$ (liquid phase composition in equilibrium with $y^*$) using Raoults law.

5. Complete the following Table.
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<tr>
<th>S.N.</th>
<th>$F$</th>
<th>$x_F$</th>
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<th>$x_D$</th>
<th>$W$</th>
<th>$x_W$</th>
<th>$y^*$</th>
<th>$x$</th>
<th>$\ln(F/W)_i$</th>
<th>$1/(y^* - x)$</th>
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6. Calculate $\ln(F/W) = \ln(F/W)_1 + \ln(F/W)_2 + \ldots + \ln(F/W)_8$

7. Plot $1/(y^* - x)$ vs $x$ and measure the area under the curve.

8. Now verify Eqn. 6

9. Calculate

$$\% \text{ Error} = \left| \frac{\ln(F/W) - \int_{x_w}^{x_F} dx/(y^* - x)}{\ln(F/W)} \right| \times 100$$