Mathematical model of batch distillation and rectification for positive and negative azeotropes

Introduction

Azeotropes occur when a real solution reveals significant deviations from Raoult’s law. There are two types of azeotropes: minimum boiling azeotrope and maximum boiling azeotrope. Each azeotrope has a characteristic boiling point. The boiling point of an azeotrope is either less than the boiling point temperatures of any of its constituents (a positive azeotrope), or greater than the boiling point of any of its constituents (a negative azeotrope). The first is encountered as a result of large positive deviation from Raoult’s law when the total vapor pressure over a liquid mixture is higher than the vapor pressure of pure, more volatile component at a given temperature. Benzene-ethanol, water-ethanol or benzene-methanol are examples of positive azeotropes. Negative azeotropes will appear for reverse situation, i.e. when the total vapor pressure over a liquid mixture is lower than that for pure, less volatile component at a given temperature. Water-hydrochloric acid, water-nitric acid or acetone-chloroform systems can be classified as negative azeotropes. Interestingly, positive azeotrope happens more often that the negative one [Anderson and Doherty, 1984; Rousseau and Fair, 1987; Pigoń and Bieganowski, 2013; Hasan et al., 2013; Bilal et al., 2014].

In a process of azeotrope rectification separation agent (entrainer) affect the relative volatility of the azeotrope constituents of the mixture. More precisely, separation agent forms such an azeotrope with the component or components of the initial mixture that separation of components with boiling points close to each other or forming other azeotropes take place. If in the new formatted azeotrope systems a region of limited miscibility arises separation of components becomes much easier [Ciborowski, 1955; Ziółkowski, 1978; Bandrowski and Trumowski, 1980].

Sobczak and Korpal [2009], Sobczak et al. [2010], Sobczak and Ringel [2013] described distillation equilibriums for both positive and negative azeotropes using the following linear relationships after determining the relative volatility (α) and concentrations of azeotropes (α) for n = 152 systems:

1. for $0 < x < \alpha$, $y > x$ and $\alpha > 1$:
   \[
   \frac{x}{y} = \frac{1}{\alpha - 1} \frac{x}{(1 - \alpha)}
   \]  
   (1)

2. for $0 < x < \alpha$, $y < x$ and $\alpha < 1$:
   \[
   \frac{y}{x} = \alpha + (1 - \alpha) \frac{y}{\alpha}
   \]  
   (2)

3. for $\alpha < x < 1$, $y > x$ and $\alpha > 1$:
   \[
   \frac{y}{x} = \frac{1}{\alpha - 1} \left(1 - \frac{1}{\alpha}ight)(y - \alpha)
   \]  
   (3)

4. for $\alpha < x < 1$, $y < x$ and $\alpha < 1$:
   \[
   \frac{x}{y} = \frac{1 - \alpha}{1 - \alpha} \left(1 - \frac{1}{\alpha}ight)(x - \alpha)
   \]  
   (4)

where: $x, y$ are concentrations of the A - comp. in the liquid and vapour.

Derivation of mathematical model

Differential balance for the $A$ component stripped in a batch rectification process expressed as $d(Sx) = yuS$, after integration gives the following form:

\[
\int_{S}^{S} \frac{dS}{\gamma} = \int_{x}^{x_0} \frac{dx^*}{\gamma x - x^*}
\]  
   (5)

For further calculations an operating line was drawn connecting points corresponding to composition of boiling liquid ($x^*$, $y^*$) on the equilibrium curve, and composition of the top product ($x_0$, $y_0$) located on diagonal $y = x (x_0 = y_0)$

\[
y - y^* = \frac{R}{R + 1} (x - x^*)
\]  
   (6)

Making use of the condition that $x = y_0$ and $y = y_0$, Eq. (6) can be rearranged into a form enabling integral (5) to be solved:

\[
y_0 - x^* = \frac{R + 1}{R + 1} (y^* - x^*)
\]  
   (7)

Substituting Eq. (7) into the integral (5) yields

\[
\ln \frac{S}{S_0} = \frac{1}{R + 1} \int_{x}^{x_0} \frac{dx^*}{y^* - x^*}
\]  
   (8)

For $x^* > x_0$: $x^* = x_0$; $y^* = y_0$; \(dx^*/(y^*-x^*) = dx/(y-x)\) and for $x^* < x_0$: $x^* = 0$; $y^* = y_0$; \(dx^*/(y^*-x^*) = - dx/(y-x)\) the following integral is obtained

\[
\ln \frac{S}{S_0} = \frac{1}{R + 1} \int_{x}^{0} \frac{dx}{y - x}
\]  
   (9)

and can be solved after substituting the equilibrium relationships $y = f(x)$ according to Eqs. (1) – (4) derived by the author of the present paper [Sobczak and Korpal, 2009; Sobczak et al., 2010; Sobczak and Ringel, 2013]. Integral (9) has been solved using the equilibrium relationships Eqs (1) – (4) to get the following model expressions for rectification process carried out at a constant reflux ratio $R = L/D$, as well as for a batch process (at $R = 0$):

For $x < a$, and $a > 1$:

\[
\frac{S}{S_0} = \frac{x}{x_0}\left(\frac{1}{x_0 - a} - \frac{1}{x - a}\right)
\]  
   (10)

For $x < a$, and $a < 1$, $\alpha = 1/a$:

\[
\frac{S}{S_0} = \frac{x}{x_0}\left(\frac{1}{x_0 - a} - \frac{1}{x - a}\right)
\]  
   (11)

After substitution of parameters $t = f(x)$ and $k = f(x_0)$ which determine concentration of the boiling liquid (1; Sobczak and Ringel, 2013) into Eqs (10) – (13) we get

For $x < a$, and $a > 1$:

\[
\frac{x}{x_0} = t\frac{x_0}{a}
\]  
   (14)

For $x < a$, and $a < 1$:

\[
\frac{x}{x_0} = t\frac{x_0}{a}
\]  
   (15)

For $x > a$, and $a > 1$:

\[
\frac{x}{x_0} = t\frac{x_0}{a}
\]  
   (16)

The universal model of batch distillation and rectification processes of positive and negative azeotropes was obtained

\[
\frac{S}{S_0} = t^\frac{1-k}{1-k} \frac{S_0}{S_0}
\]  
   (18)

\[
t = \frac{x-x_0}{x_0 - x_{in}}
\]  
   (19)

Tab. 1. Parameters of batch rectification process of azeotropes with similar values of α, \( a_{1} > 1 \) for \( c_{1} \) and \( a_{2} > 1 \) and \( k = 1/2 \)

<table>
<thead>
<tr>
<th>( a_{1} )</th>
<th>( R_{\text{lim}} )</th>
<th>( R )</th>
<th>( \alpha_{1} )</th>
<th>( \alpha_{2} )</th>
<th>( P ) [kPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Eq.(14)} = 0.48 )</td>
<td>( 1.639 )</td>
<td>1.475</td>
<td>2.22</td>
<td>0.96</td>
<td>2.22</td>
</tr>
<tr>
<td>( 0 &lt; c_{1} &lt; a_{3} )</td>
<td>0.05</td>
<td>0.375</td>
<td>0.46</td>
<td>0.75</td>
<td>2.174</td>
</tr>
<tr>
<td>( \alpha_{1} = 0.79 )</td>
<td>( a_{1}, a_{2} &lt; a_{3} )</td>
<td>1.613</td>
<td>1.452</td>
<td>2.24</td>
<td>0.58</td>
</tr>
<tr>
<td>( x_{1}(17) = 0.915 )</td>
<td>( a_{2} &lt; a_{3} &lt; 1 )</td>
<td>1.571</td>
<td>1.144</td>
<td>0.83</td>
<td>2.77</td>
</tr>
</tbody>
</table>

Tab. 2. Parameters of batch rectification process of azeotropes with different values of \( a_{1} \), \( a_{1} > 1 \) for \( a_{1} < 1 \) and \( a_{2} > 1 \) and \( k = 1/2 \)

<table>
<thead>
<tr>
<th>( x_{0} )</th>
<th>( R_{\text{lim}} )</th>
<th>( R )</th>
<th>( \alpha_{1} )</th>
<th>( \alpha_{2} )</th>
<th>( P ) [kPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Eq.(14)} = 0.48 )</td>
<td>( 2.5 )</td>
<td>2.25</td>
<td>1.8</td>
<td>0.96</td>
<td>1.8</td>
</tr>
<tr>
<td>( 0 &lt; x_{2} &lt; a_{1} )</td>
<td>0.05</td>
<td>0.375</td>
<td>0.46</td>
<td>0.75</td>
<td>1.754</td>
</tr>
<tr>
<td>( \alpha_{1} = 0.77 )</td>
<td>( a_{1} &lt; a_{2} &lt; 1 )</td>
<td>1.563</td>
<td>1.406</td>
<td>2.28</td>
<td>0.54</td>
</tr>
<tr>
<td>( \alpha_{1} = 0.83 )</td>
<td>( a_{1} &lt; a_{2} &lt; 1 )</td>
<td>1.774</td>
<td>1.596</td>
<td>0.47</td>
<td>0.66</td>
</tr>
</tbody>
</table>

The obtained results are presented in Fig. 2 and used in determining the dependences between the boiling liquid \( x_{1}, x_{2}, \) and that of distillate \( x_{2D} \) or \( x_{2D1}, x_{2D2}, \) on \( t \) as follows:

1) for \( x < a_{1} \) and \( \alpha > 1 \) \( x_{1} = t \) \( x_{0} \)

\[ x_{2D1} = x_{1} - x_{2} \]

\[ x_{2D2} = x_{2} \]

2) for \( x < a_{1} \) and \( \alpha < 1 \) \( x_{2} = f(\alpha, x_{1}) \) and \( \alpha \) = \( 1 \)

\[ x_{2D1} = x_{1} - x_{2} \]

\[ x_{2D2} = x_{2} \]

3) for \( x > a_{1} \) and \( \alpha > 1 \) \( x_{1} = t \) \( x_{1} \) \( x_{2} = x_{2} \)

\[ x_{2D1} = x_{1} \]

\[ x_{2D2} = x_{2} \]

4) for \( x > a_{1} \) and \( \alpha < 1 \) \( x_{2} = t \) \( x_{2D1} \) \( x_{2D2} \)

\[ x_{2D1} = x_{1} \]

\[ x_{2D2} = x_{2} \]

where: \( x_{2D1} \) and \( x_{2D2} \) are concentrations of distillate for the reflux ration \( R = L/D \) and \( R = 0 \)

The results are compared on Figs 3 – 6

Discussion

Mathematical models of batch distillation or rectification for positive and negative azeotropes are similar and have been derived based on considerations for vapour-liquid phase equilibrium (1 - 4). Parameters \( k \) and \( t \) (Eqs (14) – (17)) that “steer” batch distillation process [Sobczak and Ringel, 2013] control also batch rectification process. It is interesting that for all azeotropes four models of rectification and distillation processes (Eqs (10) - (13)) can be substituted by two models, 1) for \( x < a_{1} \) (Eq. (10)) and 2) for \( x > a_{1} \) (Eq. (12)) and after introducing reduced parameters \( 0 < k < 1 \) and \( 0 < t < 1 \) which determine the initial \( x_{0} \) and final concentrations \( x_{2D1}, x_{2D2} \) of azeotrope subjected to batch distillation or rectification processes and using the equivalent volatility \( \alpha_{1} = a_{1} \) when \( a_{1} > 1 \) or \( a_{1} = 1/a_{1} \) when \( a_{1} < 1 \) one universal model can be obtained (Eq. 18), which enables optimal design and control of the batch distillation and rectification processes.

Designated for rectification and distillation differential process dependancies of the concentration solution \( x = f(t) \) and distillate \( x_{2D1D2} = f(t) \), \( x_{0} = f(t) \) of the parameter are the growing functions of the \( S/S_{A} \) for the relative volatility \( \alpha > 1 \), while for \( \alpha < 1 \) are the decreasing functions of the \( S/S_{A} \) and satisfy the condition:

\[ x_{2D1} > x_{0} > x \] for \( \alpha > 1 \) and \( x_{2D2} < x_{0} < x \] for \( \alpha < 1 \]
Fig. 1. Comparison of a dependence ($S_{\text{sol}}/S_{\text{sol}}$) on parameter $t = 0.04-0.96$ (Eq. 18) obtained for rectification process at constant reflux ratio $R = 0.90R_{\text{lim}}$, with a dependence of $S_{\text{sol}}$ resulting for batch distillation process at $R = 0$ based on parameters listed in Table 1 featuring four types of azeotropes of similar equivalent volatility (2.17 < $a_1$ < 2.27) ($a_2 = a$ for $t > 1$ and $a_2 = 1/a$ for $t < 1$) for $x < a_1$ and for $x > a_1$

Fig. 2. Comparison of a dependence ($S_{\text{sol}}/S_{\text{sol}}$) on parameter $t = 0.04-0.96$ (Eq. 18) obtained for rectification process at constant reflux ratio $R = 0.90R_{\text{lim}}$, with a dependence of $S_{\text{sol}}$ resulting for batch distillation process at $R = 0$ (determining concentration of boiling solution) based on parameters listed in Table 2 featuring four types of azeotropes of similar equivalent volatility (1.754 < $a_2$ < 2.28) ($a_2 = a$ for $t > 1$ and $a_2 = 1/a$ for $t < 1$) for $x < a_1$ and for $x > a_1$

Fig. 3. Dependency statement of the parameter $t$: concentration $x_{\text{sol}}$ solution and distillate, $x_{\text{sol}}$, $x_{\text{sol}}$ (Eq. 29) and the relation ($S_{\text{sol}}/S_{\text{sol}}$) and $S_{\text{sol}}$ (Eq. 18) on the basis of the data contained in Table 2: water-acetic acid ($P = 101.32$ kPa, $x_0 = 0.48$, $a = 1.80$; $R = 0.90R_{\text{lim}} = 2.25$; $x_3$ $\alpha_3$ = 0.96)

Fig. 4. The comparison of dependency to the parameter $t$: solution concentration $x_2 = x_2(1-a)$, $x_3 = 0.42-0.21r$ and distillate $x_{\text{sol}}$, $x_{\text{sol}}$ (Eq. 30) and the relation ($S_{\text{sol}}/S_{\text{sol}}$) and $S_{\text{sol}}$ (Eq. 18) on the basis of the data in Table 2 rectification parameters: water-formic acid ($P = 101.32$ kPa, $x_0 = 0.21$, $a_1 = 1/a_1$ = 1.754; $R = 0.90R_{\text{lim}} = 2.386$; $x_3$ < $a_2$ = 0.42).

Fig. 5. Dependency statement of the parameter $t = 0.04-0.96$ concentration solution $x_{\text{sol}}(1-\alpha_1)$, $x_{\text{sol}}$ = 0.255 (0.54) and distillate, $x_{\text{sol}}$, $x_{\text{sol}}$ (Eq. 31) dependencies ($S_{\text{sol}}/S_{\text{sol}}$) and $S_{\text{sol}}$ (Eq. 18): included in Table 2 rectification parameters of water-formic acid ($P = 26.66$ kPa, $x_0 = 0.77$, $\alpha_1 = 2.28$; $R = 0.90R_{\text{lim}} = 1.40625$; $x_3$ > $a_1$ = 0.54).

Fig. 6. Dependency statement of the concentration solution $x_3 = (x_3-1)+1=0.17r$ and the distillate $x_{\text{sol}}$, $x_{\text{sol}}$ (Eq. 32) and the relation ($S_{\text{sol}}/S_{\text{sol}}$) and $S_{\text{sol}}$ (Eq. 18) from the parameter $t$ (included in Table 2 the rectification parameters: methyl acetate-methanol ($P = 101.32$ kPa, $x_0 = 0.83$, $a = 1/a = 2.128$; $R = 0.90R_{\text{lim}} = 1.596$; $x_3$ > $a_1$ = 0.66).

The limit value of the reflux $R_{\text{lim}}$ determined for the four types of azeotropes with one model (Eq. (33)) using the $k$ parameter (Eqs. (14) – (17)) and the volatility replacement $\alpha_1$ defined for the differential distillation model:

$$R_{\text{lim}} = \frac{1}{k(\alpha_1 - 1)} \tag{33}$$

LITERATURE


Hasan, S.U., Mahajani S., Malik R.K., (2013). Separation of azeotropes from the parameter $t$ (determining concentration of boiling solution) based on parameters listed in Table 2 featuring four types of azeotropes of similar equivalent volatility (1.754 < $a_2$ < 2.28) ($a_2 = a$ for $t > 1$ and $a_2 = 1/a$ for $t < 1$) for $x < a_1$ and for $x > a_1$


