**例 2** 含80%(mol)醋酸乙酯(A)和20%乙醇(E)的二元系，液相活度系数用Van Laar方程计算:

$$A_{AE} = 0.144, \qquad A_{EA} = 0.170$$

试计算：$p$=101.3kPa下的泡点温度和露点温度。

Antoine方程为 ($p^S$-Pa, $T$-K):

醋酸乙酯 $$\ln p_A^{\,s} = 21.0444 - 2790.50/(T - 57.15)$$

乙 醇 $$\ln p_E^{\,s} = 23.8047 - 3803.98/(T - 41.68)$$

该物系是理想系，完全非理想系？

汽：理想气体；液：非理想溶液。

$$K_i = \frac{\gamma_i p_i^s}{p}$$

**解：(1) 计算泡点温度**

**Step1: 计算活度系数 $\gamma_i = f(x_i)$：**

$A_{AE}$ = **0.144**, $A_{EA}$ = **0.170**

$$\ln\gamma_A = \frac{A_{AE}}{\left(1 + A_{AE}x_A / A_{EA}x_E\right)^2} = \frac{0.144}{\left(1 + 0.144\times 0.8 / 0.17\times 0.2\right)^2} = 0.0075$$

$\gamma_A$ =1.0075

$$\ln\gamma_E = \frac{A_{EA}}{\left(1 + A_{EA}x_E / A_{AE}x_A\right)^2} = \frac{0.17}{\left(1 + 0.17\times 0.2 / 0.144\times 0.8\right)^2} = 0.10137$$

$\gamma_E$ =1.1066

**Step2: 设$T_0$=353.15K**(初值设为**80℃**，**依据？**)

$$\ln p_A^s = 21.0444 - 2790.50 \big/ (353.15 - 57.15) = 11.617$$

$$\therefore \quad p_A^s = 1.1097 \times 10^5\ Pa$$

$$\ln p_E^s = 23.8047 - 3808.98 \big/ (353.15 - 41.68) = 11.5917$$

$$\therefore \quad p_E^s = 1.082 \times 10^5\ Pa$$

$$\therefore \quad K_A = \frac{\gamma_A p_A^S}{p} = \frac{1.0075 \times 1.1097 \times 10^5}{101325} = 1.1034$$

$$K_E = \frac{\gamma_E P_E^S}{P} = \frac{1.1066 \times 1.082 \times 10^5}{101325} = 1.1817$$

$$\sum K_i x_i = 1.1034 \times 0.8 + 1.1817 \times 0.2 = 1.1191$$

## Step3:由修正平衡常数法

$$K_A^{(1)}=\frac{K_A^{(0)}}{\sum K_i^{(0)}x_i}$$

**调整** $K_A^{(1)}=1.1034/1.1191=0.98597$

$$p_{A2}^S=\frac{K_A^{(1)}p}{\gamma_A}=\frac{0.98597\times101325}{1.0075}=exp(21.0444-\frac{2790.5}{T-57.15})$$

**解得$T_1$=349.66K，即$T_1$=76.51℃**

$\therefore$ $p_A^s=9.9166\times10^4\,Pa$ $p_E^s=9.4213\times10^4\,Pa$

$K_A^{(1)}$ =0.98597 $K_E^{(1)}$ =1.0289

$$\sum K_i^{(1)}x_i=0.98597\times0.8+1.0289\times0.2=0.9946\approx1$$

$\therefore$

**故泡点温度为76.51℃**

## (2) 计算露点温度

则已知 $y_A = 0.8; y_E = 0.2$

$x_i$未知，设活度系数初始值 $\gamma_A^{(0)}=1$，$\gamma_E^{(0)}=1$

设$T_0$=353.15K(80°C)，则：

$$K_A = \frac{\gamma_A p_A^S}{p} = \frac{1\times1.1097\times10^5}{101325} = 1.0952$$

$$K_E = \frac{\gamma_E p_E^S}{p} = \frac{1\times1.082\times10^5}{101325} = 1.0678$$

$$\sum x_i = \sum \frac{y_i}{K_i} = \frac{0.8}{1.0952} + \frac{0.2}{1.0678} = 0.9178 \neq 1$$

$$x_i = \frac{y_i}{K_i}$$

$x_{A1} = 0.7305$　$x_{E1} = 0.1873$

归一化，圆整得　$x_{A1} = 0.7959$　$x_{E1} = 0.2041$

代入Van Laar方程，得：

$$\ln\gamma_A=\frac{A_{AE}}{\left(1+\dfrac{A_{AE}x_A}{A_{EA}x_E}\right)^2}=\frac{0.144}{\left(1+\dfrac{0.144\times 0.7959}{0.170\times 0.2041}\right)^2}=0.00778$$

$$\gamma_A^{(1)}=1.0078$$

$$\ln\gamma_E=\frac{A_{EA}}{\left(1+\dfrac{A_{EA}x_E}{A_{AE}x_A}\right)^2}=\frac{0.170}{\left(1+\dfrac{0.170\times 0.2041}{0.144\times 0.7959}\right)^2}=0.10017$$

$$\gamma_E^{(1)}=1.1054$$

由

$$K_A^{(1)}=K_A^{(0)}\times\sum\frac{y_i}{K_i^{(0)}}$$

$$K_A^{(1)}=1.0952\times 0.9178=1.0052$$

$$p_A^{S(1)} = \frac{K_A^{(1)} p}{\gamma_A^{(1)}} = \frac{1.0052 \times 101325}{1.0078} = 1.01064 \times 10^5 = \exp(21.0444 - \frac{2790.5}{T - 57.15})$$

**解得$T_1$ =350.25K(77.1°C)**

$\ln p_A^{s\,(1)}$ =11.523, $\quad p_A^{s\,(1)} = 1.0109 \times 10^5$ Pa

$\ln p_E^{s\,(1)}$ =11.477, $\quad p_E^{s\,(1)} = 9.6464 \times 10^4$ Pa

$$K_A^{(1)} = \frac{\gamma_A^{(1)} p_A^{S(1)}}{p} = 1.0055 \qquad K_E^{(1)} = \frac{\gamma_E^{(1)} p_E^{S(1)}}{p} = \frac{1.1054 \times 9.6464 \times 10^4}{101325} = 1.0524$$

$$\sum x_i = \sum \frac{y_i}{K_i} = 0.8/1.0055 + 0.2/1.0524 = 0.9857 \neq 1$$

$$x_i = \frac{y_i}{K_i}$$

$x_{A1} = 0.7956$ $\quad x_{E1} = 0.1900$

归一化，圆整得 $x_{A1} = 0.8072$ $\quad x_{E1} = 0.1928$

代入Van Laar方程，得：

$$\ln\gamma_A=\frac{A_{AE}}{\left(1+\frac{A_{AE}x_A}{A_{EA}x_E}\right)^2}=\frac{0.144}{\left(1+\frac{0.144\times0.8072}{0.170\times0.1928}\right)^2}=0.00697$$

$$\gamma_A^{(1)}=1.0070$$

$$\ln\gamma_E=\frac{A_{EA}}{\left(1+\frac{A_{EA}x_E}{A_{AE}x_A}\right)^2}=\frac{0.170}{\left(1+\frac{0.170\times0.1928}{0.144\times0.8072}\right)^2}=0.10344$$

$$\gamma_E^{(1)}=1.1090$$

由

$$K_A^{(2)}=K_A^{(1)}\times\sum\frac{y_i}{K_i^{(1)}}$$

$$K_A^{(2)}=1.0055\times0.9857=0.9911$$

$$p_A^{s(2)} = \frac{K_A^{(2)} p}{\gamma_A^{(2)}} = \frac{0.9911 \times 101325}{1.0070} = 9.9725 \times 10^4 = \exp(21.0444 - \frac{2790.5}{T - 57.15})$$

解得$T_1$ =349.83K(76.68℃)

$$\ln p_A^{s(2)} = 11.510, \quad p_A^{s(2)} = 9.9717 \times 10^4 \text{ Pa}$$

$$\ln p_E^{s(2)} = 11.460, \quad p_E^{s(2)} = 9.4857 \times 10^4 \text{ Pa}$$

$$K_A^{(2)} = \frac{\gamma_A^{(2)} p_A^{S(2)}}{p} = 0.9910 \qquad K_E^{(2)} = \frac{\gamma_E^{(2)} p_E^{S(2)}}{p} = \frac{1.1090 \times 9.4857 \times 10^4}{101325} = 1.0382$$

$$\sum x_i = \sum \frac{y_i}{K_i} = 0.8/0.9910 + 0.2/1.0382 = 0.9999 \to 1$$

故露点温度为$T=T_1$=349.83K(76.68℃)。

$$x_i = \frac{y_i}{K_i}$$

$x_{A1} = 0.8073$ $x_{E1} = 0.1927$ 与上轮迭代相比，液相组成也趋于恒定