第2章多组分精馏 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 例 2 Laar方程计算:

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

$$A_{EA} = 0.170$$

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):

$$(p^{S}-Pa, T-K)$$
:

$$\ln p_A^S = 21.0444 - \frac{2790.50}{(T - 57.15)}$$

乙醇

$$\ln p_E^S = 23.8047 - \frac{3803.98}{(T - 41.68)}$$

该物系是理想系,完全非理想系?

汽:理想气体;液:非理想溶液。

解: (1) 计算泡点温度

Step1: 计算活度系数 $\gamma_i = f(x_i)$:

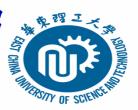
 $\gamma_E = 1.1066$

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

$$\ln \gamma_{A} = \frac{A_{AE}}{(1 + A_{AE} x_{A}/A_{EA} x_{E})^{2}} = \frac{A_{AE}}{(1 + 0.144 \times 0.8/0.17 \times 0.2)^{2}} = 0.0075$$

$$\gamma_{A} = 1.0075$$

$$\ln \gamma_{E} = \frac{A_{EA}}{(1 + A_{EA} x_{E}/A_{AE} x_{A})^{2}} = \frac{0.17}{(1 + 0.17 \times 0.2/0.144 \times 0.8)^{2}} = 0.10137$$



Step2: 设T₀=353.15K(初值设为80℃,依据?)

$$\ln p_A^s = 21.0444 - \frac{2790.50}{(353.15 - 57.15)} = 11.617$$

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

$$ln p_E^s = 23.8047 - \frac{3808.98}{(353.15 - 41.68)} = 11.5917$$

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

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

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

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



Step3:由修正平衡常数法

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

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

$$p_{A2}^{S} = \frac{K_A^{(1)}p}{\gamma_A} = \frac{0.98597 \times 101325}{1.0075} = exp(21.0444 - \frac{2790.5}{T - 57.15})$$

解得T₁=349.66K, 即T₁=76.51℃

$$p_A^s = 9.9166 \times 10^4 Pa$$

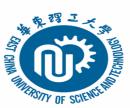
$$p_E^s = 9.4213 \times 10^4 Pa$$

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

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

$$\sum K_i^{(1)} x_i = 0.98597 \times 0.8 + 1.0289 \times 0.2 = 0.9946 \approx 1$$

故泡点温度为76.51°C



(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T₀=353.15K(80°C),则:

$$K_A = \frac{\gamma_A p_A^S}{p} = \frac{1 \times 1.1097 \times 10^5}{101325} = 1.0952$$

$$K_E = \frac{\gamma_E p_E^S}{p} = \frac{1 \times 1.082 \times 10^5}{101325} = 1.0678$$

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

$$x_{i} = \frac{y_{i}}{K_{i}}$$
 $x_{A1} = 0.7305$ $x_{E1} = 0.1873$

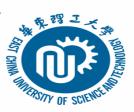
$$x_{A1} = 0.7305$$

$$x_{E1} = 0.1873$$

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

$$x_{A1} = 0.7959$$

$$x_{E1} = 0.2041$$



代入Van Laar方程,得:

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

$$\gamma_{A}^{(1)} = 1.0078$$

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

$$\gamma_{\rm E}^{\ (1)} = 1.1054$$

$$\mathbf{H}_{A}^{(1)} = \mathbf{K}_{A}^{(0)} \times \sum \frac{\mathbf{y}_{i}}{\mathbf{K}_{i}^{(0)}}$$

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

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

解得T₁=350.25K(77.1°C)

$$\ln p_A^{s}$$
 =11.523,

$$\ln p_E^{s}$$
 =11.477,

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

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

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

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

$$\mathbf{x}_{i} = \frac{\mathbf{y}_{i}}{\mathbf{K}_{i}} \qquad \mathbf{x}_{A1} = \mathbf{0.7956} \qquad \mathbf{x}_{E1} = 0.1900$$

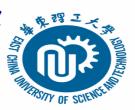
$$x_{A1} = 0.7956$$

$$\mathbf{x}_{E1} = 0.1900$$

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

$$x_{A1} = 0.8072$$

$$x_{E1} = 0.1928$$



代入Van Laar方程,得:

$$\ln \gamma_A = \frac{A_{AE}}{\left(1 + \frac{A_{AE} x_A}{A_{EA} x_E}\right)^2} = \frac{0.144}{\left(1 + \frac{0.144 \times 0.8072}{0.170 \times 0.1928}\right)^2} = 0.00697$$

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

$$\ln \gamma_E = \frac{A_{EA}}{\left(1 + \frac{A_{EA} x_E}{A_{AE} x_A}\right)^2} = \frac{0.170}{\left(1 + \frac{0.170 \times 0.1928}{0.144 \times 0.8072}\right)^2} = 0.10344$$

$$\gamma_{\rm E}^{(1)} = 1.1090$$

由

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

$$K_A^{(2)} = 1.0055 \times 0.9857 = 0.9911$$

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

解得T₁=349.83K(76.68°C)

$$ln p_A^{s}^{(2)} = 11.510,$$

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

$$ln p_E^{s(2)} = 11.460,$$

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

$$K_A^{(2)} = \frac{\gamma_A^{(2)} p_A^{S^{(2)}}}{p} = 0.9910$$

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

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

故露点温度为T=T₁=349.83K(76.68℃)。

$$\boldsymbol{x}_{i} = \frac{\mathbf{y}_{i}}{\boldsymbol{K}_{i}}$$

$$\mathbf{x}_{\Delta 1} = \mathbf{0.8073}$$

$$\mathbf{x}_{\mathrm{E1}} = 0.1927$$

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