SUPPORTING INFORMATION

Appendix A: Scaled particle theory for ethyl acetate (1) - ethanol (2) – salt (3) system

The theory illustrates the principle of extractive distillation to separate an azeotrope using salt as third component. The system under consideration consists of the following two solvents combined with salt, [1] Ethyl acetate, [2] Ethanol. The subscripts 1, 2, 3 & 4 are used to represent ethyl acetate, ethanol, cation of the salt and anion of the salt respectively.

For 1:1 electrolyte,

Expression for k_γ:-

$$\sum \rho_i = \rho_1 + \rho_2 + \rho_3 + \rho_4 \qquad \text{(A.1)}$$

Neglecting ρ_1, we get the following equation,

$$\sum \rho_i = \rho_2 + \rho_3 + \rho_4 \qquad \text{(A.2)}$$

$$\rho_2 = \frac{Nd_2}{M_2}\left(1 - \frac{c\phi}{1000}\right)$$

$$\rho_3 = \rho_4 = \frac{Nc}{1000}$$

Where, M_2 represents molecular weight of ethanol = 46.07 g/mol, d_2 represents density at 25^{o}C=785.22 kg.m^{-3}, ϕ^0 represents apparent molal volume of salt at infinite dilution at 25 ^{o}C

$$\ln \sum \rho_i = \ln \frac{Nd_2}{M_2}\left[1 - \frac{c\phi}{1000} + \frac{2cM_2}{1000d_2}\right] \qquad \text{(A.3)}$$

$$\frac{1}{2.3}\ln \sum \rho_i = \frac{1}{2.3}\ln \frac{Nd_2}{M_2}\left[1 - \frac{c\phi}{1000} + \frac{2cM_2}{1000d_2}\right]$$

$$k_\gamma = \left[\frac{d}{dc}\log \sum \rho_i\right]_{c \to 0} = \frac{2M_2}{2300d_2} - \frac{\phi}{2300} \qquad \text{(A.4)}$$

After substitution of values, we get,

$$k_\gamma = 0.0510 - 4.34 \times 10^{-4}\phi \qquad \text{(A.5)}$$

Expression for k_β:-

$$\frac{\bar{g}_1^{\,s}}{2.3kT}=\frac{-32\pi Nc}{9000(2.3T)}\left[\frac{\varepsilon_{13}\sigma_{13}^3}{k}+\frac{\varepsilon_{14}\sigma_{14}^3}{k}\right]-\frac{4\pi Nd_2}{3(2.3T)M_2}\left[1-\frac{c\phi}{1000}\right]\left[\frac{8\varepsilon_{12}\sigma_{12}^3}{3k}+\frac{\mu_2^2\alpha_1}{k\sigma_{12}^3}\right] \qquad (A.6)$$

Considering the first derivative of the above equation with respect to 'C' and by further simplification we arrive at,

$$k_\beta=\frac{d}{dc}\left[\frac{\bar{g}_1^{\,s}}{2.3kT}\right]_{c\to 0} =$$

$$-9.8095\times10^{18}\left[\frac{\varepsilon_{13}\sigma_{13}^3}{k}+\frac{\varepsilon_{14}\sigma_{14}^3}{k}\right]+1.6719\times10^{17}\phi\left[\frac{\varepsilon_{12}\sigma_{12}^3}{k}\right]+\frac{4\pi Nd_2\mu_2^2}{3000(2.3T)M_2\sigma_{12}^3} \qquad (A.7)$$

Taking μ_2=1.69E-18 cm; T=298K,

The mixture parameters must be related to those parameters of the pure species. Hence we use a rule which is known as the "mixing rule", by which,

$$\varepsilon_{ij}=\left(\varepsilon_i\varepsilon_j\right)^{\frac{1}{2}};\sigma_{ij}=\frac{\sigma_i+\sigma_j}{2}$$

And thereby assign a numerical value for k_β. The numerical value for the energy parameter $\frac{\varepsilon_1}{k}$ = 450.

Also the values of ε/k for the cation and anion of the salt can be obtained by using Mavroyannis-Stephen equation, given as,

$$\frac{\varepsilon_j}{k}=2.28\times10^{-8}\,\frac{\alpha_j^{\frac{3}{2}}z_j^{\frac{1}{2}}}{\sigma_j^6}$$

$$k_\beta = -1.85\times10^{14}\left(\frac{\varepsilon_1}{k}\right)^{\frac{1}{2}}\left[\alpha_3^{\frac{3}{4}} z_3^{\frac{1}{4}}\left(\frac{\sigma_1+\sigma_3}{\sigma_3}\right)^3 + \alpha_4^{\frac{3}{4}} z_4^{\frac{1}{4}}\left(\frac{\sigma_1+\sigma_4}{\sigma_4}\right)^3\right]$$

$$+4.43\times10^{17}\phi\left(\frac{\varepsilon_1}{k}\right)^{\frac{1}{2}}\left(\sigma_1+\sigma_2\right)^3 + 1.03\times10^{-2}\frac{\phi\alpha_1}{\left(\sigma_1+\sigma_2\right)^3} \quad \text{(A.8)}$$

Expression for k_α:-

The expression for free energy of cavity formation according to Scaled Particle Theory is as follows,

$$\frac{\bar{g}_1^{\,h}}{2.3kT} = -\log\left(1-\tau_3\right)+A \quad \text{(A.9)}$$

$$A = \frac{3\tau_2\sigma_1}{2.3\left(1-\tau_3\right)}\left[1+\frac{\tau_1\sigma_1}{\tau_2}+\frac{3\tau_2\sigma_1}{2\left(1-\tau_3\right)}\right]$$

$$\tau_n = \frac{\pi}{6}\sum_1^n \rho_j\sigma_j^n \quad \text{(A.10)}$$

$$\tau_1 = \frac{\pi}{6}\frac{Nd_2\sigma_2}{M_2} + c\left[\frac{\pi}{6}\frac{N}{1000}\left(\sigma_3+\sigma_4\right) - \frac{\pi}{6}\frac{Nd_2\sigma_2}{M_2}\frac{\phi}{1000}\right]$$

On substitution of values namely,

$$\tau_1 = 2.33\times10^{14} + c\left[3.15\times10^{20}\left(\sigma_3+\sigma_4\right) - 2.33\times10^{11}\phi\right]$$

$$\tau_2 = 1.012\times10^7 + c\left[3.15\times10^{20}\left(\sigma_3^2+\sigma_4^2\right) - 1.012\times10^4\phi\right]$$

$$\tau_3 = 0.439 + c\left[3.15\times10^{20}\left(\sigma_3^3+\sigma_4^3\right) - 4.393\times10^{-4}\phi\right]$$

$$\ln\tau_1 - \ln\tau_2 = \ln\left(2.33\times10^{14} - 1.012\times10^7\right) + 1351931.33\left(\sigma_3+\sigma_4\right)c - 3.113\times10^{13}\left(\sigma_3^2+\sigma_4^2\right)c$$

$$\frac{\tau_1}{\tau_2} = 2.30\times10^7 + c\left[3.113\times10^{13}\left(\sigma_3+\sigma_4\right) - 7.16\times10^{20}\left(\sigma_3^2+\sigma_4^2\right)\right]$$

$$\frac{\tau_2}{1-\tau_3} = 1.80\times10^7 + c\left[5.59\times10^{20}\left(\sigma_3^2+\sigma_4^2\right) + 1.01\times10^{28}\left(\sigma_3^3+\sigma_4^3\right) - 3.21\times10^4\phi\right]$$

$$A = \frac{3\tau_2\sigma_1}{2.3\left(1-\tau_3\right)}\left[1+\frac{\tau_1\sigma_1}{\tau_2}+\frac{3\tau_2\sigma_1}{2\left(1-\tau_3\right)}\right] \quad \text{(A.11)}$$

$$= 2.35\times10^{7}\sigma_1 + c\sigma_1\left[7.29\times10^{20}\left(\sigma_3^2+\sigma_4^2\right)+1.32\times10^{28}\left(\sigma_3^3+\sigma_4^3\right)-4.19\times10^{4}\phi\right]$$
$$+c\sigma_1^2\left[7.31\times10^{20}\left(\sigma_3+\sigma_4\right)+3.94\times10^{28}\left(\sigma_3^2+\sigma_4^2\right)+1.02\times10^{36}\left(\sigma_3^3+\sigma_4^3\right)-3.23\times10^{12}\phi\right]$$

$$k_\alpha = \left[\frac{d\left[\log\left(1-\tau_3\right)\right]}{dc}+\frac{dA}{dc}\right]_{c\to0}$$

$$k_\alpha = 2.44\times10^{20}\left(\sigma_3^3+\sigma_4^3\right)-3.40\times10^{-4}\phi+\sigma_1\left[7.29\times10^{20}\left(\sigma_3^2+\sigma_4^2\right)+1.32\times10^{28}\left(\sigma_3^3+\sigma_4^3\right)-4.19\times10^{4}\phi\right]$$
$$+\sigma_1^2\left[7.31\times10^{20}\left(\sigma_3+\sigma_4\right)+3.94\times10^{28}\left(\sigma_3^2+\sigma_4^2\right)+1.02\times10^{36}\left(\sigma_3^3+\sigma_4^3\right)-3.23\times10^{12}\phi\right]$$

(A.12)

For 1:2 electrolyte,

The following derivation is done on the same basis as that of the system containing a 1:1 electrolyte and the corresponding expressions for $k_\alpha, k_\beta, k_\gamma$ are obtained. The only difference is that the system considered here, is composed of two moles of anion and one mole of cation thereby leading to a change in density of a solution.

Expression for k_γ:-

$$\rho_2 = \frac{Nd_2}{M_2}\left(1-\frac{c\phi}{1000}\right), \qquad \rho_3 = \frac{Nc}{1000},$$

$$\rho_4 = \frac{2Nc}{1000}$$

$$k_\gamma = \frac{3M_2}{2300d_2}-\frac{\phi}{2300}$$

(A.13)

Expression for k_β:-

$$k_\beta = 1.8515\times10^{14}\left(\frac{\varepsilon_1}{k}\right)^{\frac{1}{2}}\left[\alpha_3^{\frac{3}{4}}z_3^{\frac{1}{4}}\frac{\left(\sigma_1+\sigma_3\right)^3}{\sigma_3^3}+\alpha_4^{\frac{3}{4}}z_4^{\frac{1}{4}}\frac{\left(\sigma_1+\sigma_4\right)^3}{\sigma_4^3}\right]$$

$$+4.433\times10^{17}\phi\left(\frac{\varepsilon_1}{k}\right)^{\frac{1}{2}}\left(\sigma_1+\sigma_2\right)^3+1.038\times10^{-2}\frac{\phi\alpha_1}{\left(\sigma_1+\sigma_2\right)^3}$$

(A.14)

Expression for k_α:-

$$k_\alpha = 7.32\times10^{20}\left(\sigma_3^3+\sigma_4^3\right)-3.40\times10^{-4}\phi+\sigma_1\left[2.19\times10^{21}\left(\sigma_3^2+\sigma_4^2\right)+3.96\times10^{28}\left(\sigma_3^3+\sigma_4^3\right)-4.19\times10^{4}\phi\right]$$
$$+\sigma_1^2\left[2.19\times10^{21}\left(\sigma_3+\sigma_4\right)+1.18\times10^{29}\left(\sigma_3^2+\sigma_4^2\right)+3.05\times10^{36}\left(\sigma_3^3+\sigma_4^3\right)-3.23\times10^{12}\phi\right]$$

(A.15)

NOMENCLATURE

c	Concentration of salt, mol/l
k_s	Salting coefficient
$k_\alpha, k_\beta, k_\gamma$	Contributions to salting coefficient
M	Molecular weight (g/mol)
N	Avogadro number
S	Solubility of non-electrolyte in salt solution
S_o	Solubility of non-electrolyte in pure water
T	Temperature, °C
x'_i	Salt free mole fraction of component i in liquid
y_i	mole fraction of component i in Vapor
z	Salt mole fraction
γ_i	activity coefficient of component i in liquid
α_1	Polarizability of non-electrolyte
ρ_i	Density of the components (g/cc)
σ	molecule size or ion diameter (˚A)
ϕ°	apparent molal volume of salt at infinite dilution (cc/mol)
ε/k	interaction energy parameter (K)