Tutorial 8 – training problem.

Figure 1* shows an example ternary phase diagram. In this example, component A is partially miscible in components B and C, while components B and C are not miscible in each other. The composition of each component increases towards 100% as one approach its vertex. When multiphase systems are observed in a ternary phase diagram, the composition of the phases (β and γ in the example) in equilibrium is connected by a tie line, which represents the process of separation of the multiphase system.

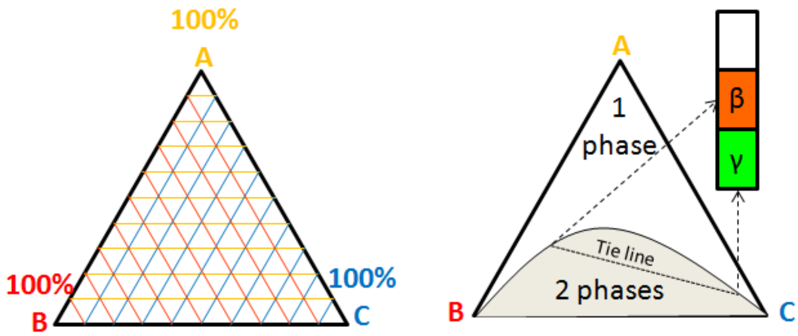

Figure 1* Ternary phase diagram composition lines (left) and example ternary phase diagram displaying a multiphase region and a composition tie line.

In the design of formulations for cosmetics, detergents, pharmaceutics, and in the design of solvents, it is often enough to map the 1 phase region, which is often the target region for the formulation. To design extraction processes, you also need to know the composition of the phases in equilibrium. This means, you also need to determine the tie lines for the multiphase system. Common applications of liquid-liquid extraction processes include: recovery of hydrophobic components from aqueous phase: such components include phenol, aniline, glycols, amines, formaldehyde, formic acid, acetic acid, penicillin, glycerol (from biodiesel production), halogenated solvents, caprolactam and adiponitrile (for nylon production), and many others.

For the ternary phase diagram presented below for ethanol (component 1) – toluene (component 2)- water (component 3) {Figure 14 from the article: IUPAC-NIST solubility data series 69. Ternary alcohol-hydrocarbon-water systems. J. Phys. Chem. Ref. Data, 28(4), 1999}, determine:

a) The composition of the feed (red point) to a liquid-liquid extractor (think of it as the equivalent to the feed of a flash separator, only that here you separate two liquid phases instead of separating a liquid and a vapour phase).

b) The composition of the two liquid phases in equilibrium that are produced after the separation takes place. Determine the partition of ethanol (molar fraction of ethanol in aqueous phase/molar fraction of ethanol in the toluene-rich phase).

c) Considering that the Henry's constant for ethanol in water at 25°C is 29.7kPa , and that toluene-ethanol forms an azeotrope at 76.7°C, 1 atm when the weight fraction of toluene is 0.32. Estimate the partition coefficient (on the basis of molar fractions) of ethanol between water and toluene at infinite ethanol dilution.

Additional information:

$\ln (P^{\circ}_{ethanol,kPa}) = 16.69-3681.7/(T_{°C}+226.58)$; MW = 46 g/mol

$\ln (P^{\circ}_{toluene,kPa}) = 14.01-3100.7/(T_{°C}+219.49)$; MW= 92 g/mol

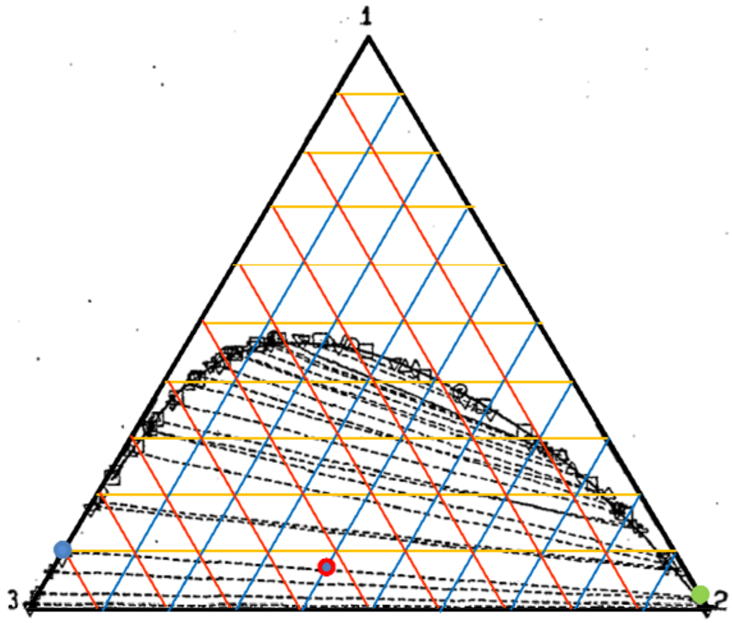

FIG. 14. Phase diagram of the system ethanol (1)—toluene (2)—water (3) at 298.2 K. Solid line—calculated saturation curve, ◇—experimental data, Ref. 10, ○—experimental data, Ref. 3, ✣—experimental data, Ref. 11, □—experimental data, Ref. 5, ▽—experimental data, Ref. 12, △—experimental data, Ref. 7, dashed lines—experimental tie lines, Refs. 7, 11, and 12.

Solution

a) Composition of the feed => we follow the yellow lines from the bottom base of the triangle 0% ethanol to the top vertex (vertex 1). The first yellow line is 10wt% ethanol. We notice that the composition of ethanol in the feed (the red point) is close to 8 wt% ethanol. To read the toluene content (component 2), we follow the blue lines, starting from the left base towards the right vertex (vertex 2). From that direction, then the fourth blue line represents 40 wt% of toluene. To read the water content (component 3) we start from the right base of the triangle towards the left vertex (vertex 3). In this case, the point that sits just after the fifth red line, corresponds to a water content of about 52wt%. We could also have said that the water content was 100-40-8% and would have arrived to the same conclusion.

b) The composition of the two liquid phases in equilibrium. To read the compositions in equilibrium we need to follow the tie line that passes through the feed to the separator (the red point). Following this tie line will lead us to two phases, one a phase rich in toluene (towards vertex 2), represented by the green dot, and a phase rich in water (towards vertex 3) represented by the blue dot.
The composition for the toluene-rich phase: ~ 2wt% ethanol, and 98 wt% toluene.
The composition for the aqueous phase: ~ 10wt% ethanol, and 90 wt% water.

To figure out the partition coefficient in terms of molar fractions, we need
$x_{\text{ethanol, toluene phase}}$ = (2g/46g/mol)/(2g/46g/mol+98g/92g/mol) = 0.0392
$x_{\text{ethanol, aqueous}}$ = (10g/46g/mol)/(10g/46g/mol+90g/18g/mol) = 0.0417
Then $K_{eq} = x_{\text{ethanol, aqueous}} / x_{\text{ethanol, toluene phase}}$ = 0.0417/0.0392 = 1.06

From the Henry's constant we can calculate the Margules 1-parameter for ethanol and water:

$P°_{ethanol,kPa,\ 25°C}$ = exp(16.69-3681.7/(25+226.58)) = 7.81 kPa
$A_{ethanol\text{-}water}$ = ln(H/$P°_{ethanol}$) =ln(29.7/7.81) = 1.34 (this equation was derived in class).

From the azeotrope, we can calculate the Margules 2-parameters between ethanol and toluene.

toluene-ethanol forms an azeotrope at 76.7°C, 1 atm when the weight fraction of toluene is 0.32. Estimate the partition coefficient (on the basis of molar fractions) of ethanol between water and toluene.
Additional information:

$P°_{ethanol,kPa,\ 76.7°C}$ = exp(16.69-3681.7/(76.7+226.58)) = 94.67 kPa
$P°_{toluene,kPa,\ 76.7°C}$ = exp(14.01-3100.7/(76.7+219.49)) = 34.52 kPa
$x_{toluene,\ az}$ = (32/92)/(32/92+68/46) = 0.19
$x_{wthanol,\ az}$ = 1- 0.19=0.81

From the condition of the Azeotrope (see previous tutorial for the condition $\gamma_{i,azeotrope} = P/\ P_i°$)
$\gamma_{ethanol,azeotrope} = P/\ P_{ethanol}°$ = 101.3kPa/94.67 kPa = 1.07
$\gamma_{toluene,azeotrope} = P/\ P_{toluene}°$ = 101.3kPa/34.52 kPa = 2.9345
The Margules 2-parameter equation are:
$\gamma_1 = \exp(x_2^2(A_{12} + 2(A_{21}-A_{12})x_1)$ and $\gamma_2 = \exp(x_1^2(A_{21} + 2(A_{12}-A_{21})x_2)$
$A_{12} = 2\ln(\gamma_{2,az})/x_{1,az} - \ln(\gamma_{1,az})(x_{1,az} - x_{2,az})/x_{2,az}^2$
$A_{21} = 2\ln(\gamma_{1,az})/x_{2,az} - \ln(\gamma_{2,az})(x_{2,az} - x_{1,az})/x_{1,az}^2$
Component 1=> ethanol, 2=> toluene
Therefore:
A_{12} = 2*ln(2.93)/0.81 - ln(1.07)*(0.81 –(1-0.81))/(1-0.81)^2 = 1.49
This is the interaction parameter that dominates a situation where there is a little bit of ethanol in a lot of toluene.
A_{21} = 2*ln(1.07)/(1-0.81) - ln(2.93)*((1-0.81)– 0.81)/0.81^2 = 1.73
This is the interaction parameter that dominates a situation where there is a little bit of toluene in a lot of ethanol.

As per the ternary phase diagram, at equilibrium we have one aqueous phase that has a little bit of ethanol and no toluene (in which case, the interaction $A_{ethanol\text{-}water}$ obtained from Henry's law is suitable), and in the other case we have a toluene-rich phase that has a little bit of ethanol and no water (In that case, the interaction parameter A_{12}=1.49 is the suitable one).
According to the equilibrium of ethanol: $x_{ethanol,aq} * \gamma_{ethanol,aq} = x_{ethanol,tol} * \gamma_{ethanol,tol}$
Then Keq = $x_{ethanol,aq}/\ x_{ethanol,tol} = \gamma_{ethanol,tol}/\ \gamma_{ethanol,aq}$
Where $\gamma_{ethanol,tol} = \exp(x_{toluene,tol}^2(A_{12} + 2(A_{21}-A_{12})x_{ethanol,tol})$ but considering infinite ethanol dilution, $x_{ethanol,tol} \sim 0$, and $x_{toluene,tol} \sim 1$ then $\gamma_{ethanol,tol} = \exp(A_{12})$
Where $\gamma_{ethanol,aq} = \exp(x_{watert,aq}^2(A_{ethanol\text{-}water}))$ but considering infinite ethanol dilution, $x_{ethanol,aq} \sim 0$, and $x_{water,aq} \sim 1$ then $\gamma_{ethanol,aq} = \exp(A_{ethanol\text{-}water})$
Then Keq = $x_{ethanol,aq}/\ x_{ethanol,tol} = \gamma_{ethanol,tol}/\ \gamma_{ethanol,aq} = \exp(A_{12})/\exp(A_{ethanol\text{-}water})$
$K_{eq,\ infinite\ dilution}$ = exp(1.49)/exp(1.34) = 1.16
This partition constant compares well with the partition coefficient of 1.06 obtained from the data of the ternary phase diagram.