Mass Transfer Operations II

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Lecture No. 11

Effect of temperature on liquid-liquid equilibria & Design calculation of single stage extraction

Welcome back to Mass Transfer Operations II course, we were discussing on liquid-liquid extraction now we will be discussing on the effect of temperature on liquid-liquid equilibria and design calculation of single state extraction.

Effect of temperature on LLE:

Effect of temperature is very strong. Miscibility of a liquid pair generally increases with temperature. Miscibility of B-C pair increases more rapidly than that of A-B pair (TYPE II system). T the critical solution temperature of a B-C pair, a TYPE II system turns into a TYPE I system. The two phase region of the equilibrium diagram for a TYPE II system still contracts with increasing temperature and eventually vanishes at a temperature called its “critical solution temperature” t_{CS}. The critical solution temperature is the minimum temperature at which the component A, B and C of a TYPE I system becomes miscible in all proportions.

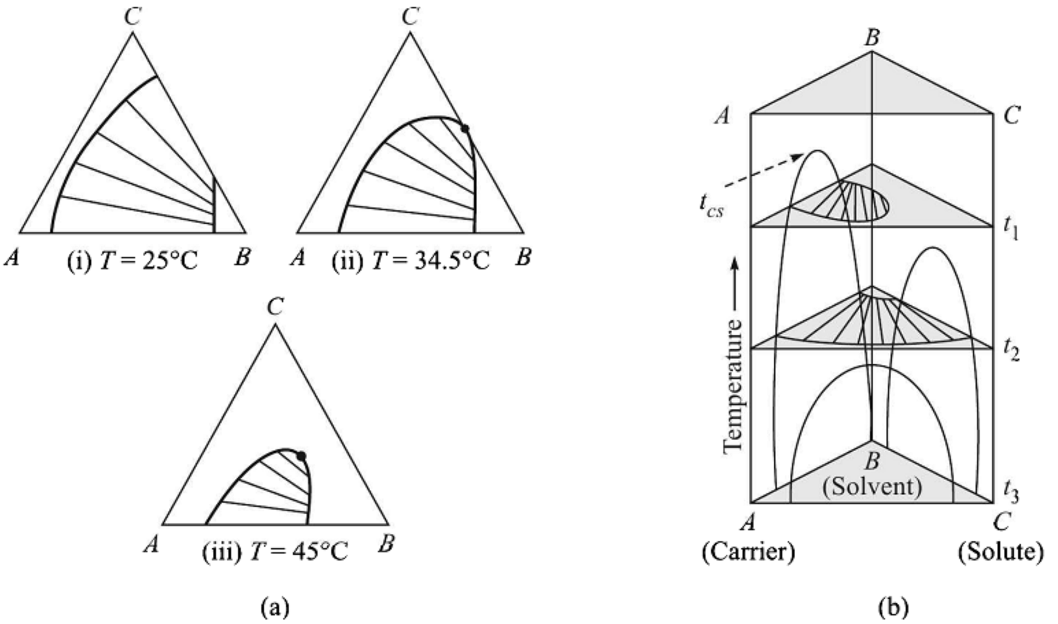


Figure 8: Effect of temperature on ternary equilibrium.

Solvent selection:

The right solvent is the key to successful separation by solvent extraction. Solvents are mostly organic. The important criteria for solvent selection are given below:

(a) Selectivity: Selectivity or preferential uptake of the solute by the solvent over the carrier is most important factor.

Selectivity is defined as: $\beta_{C,A} = (y_C / y_A) / (x_C / x_A) = {}^{y}{}_{E}^{*}/x_R$

Where:

y_E is the wt. fraction of C in E

y_A is the wt. fraction of A in E

x_C is the wt. fraction of C in R

x_A is the wt. fraction of A in R

y_E^* is the wt. fraction of A in E

x_R is the wt. fraction of A in R

(b) Carrier solvent immiscibility: If the mutual solubility of the carrier and the solvent is low, they can be satisfactorily separated in the settler. Only a small quantity of solvent will be retained in raffinate and small quantity of carrier will remain dissolved in solvent. So cost of further separation of the phases by distillation or otherwise will be small.

(c) Interfacial tension: interfacial tension between carrier and solvent has two opposing effects. A low interfacial tension favours fine dispersion of one liqid in the other, thereby increasing the specific interfacial area of mass transfer. On the other hand coalescence of droplets leading to the separation of the raffinate and the extract phases does not occur readily if the interfacial tension is low.

(d) Density: The driving force for phase separation (in settler) is the difference in densities of two phases. The density of light phase should be at least 5% less tan that of the heavier phase in order to ensure smooth phase separation.

(e) Viscosity, vapour pressure and freezing point: These should be low for ease in handling and storage.

(f) Chemical reactivity: The solvent should be inert and chemically stable.

(g) Recoverability: It is always necessary to recover the solvent for reuse and must be done by another mass transfer operation, e.g. distillation. Solvent should not form azeotrope with extracted solute.

(h) Distribution coefficient: y^*/x at equilibrium >1 or large values are desirable since less solvent will be required for extraction.

(i) The solvent should be non-toxic, non-flammable and of low cost.

(j) Accumulation of impurities: Accumulation of impurities is observed if solvent is of low volatility. It lowers interfacial-tension and surface resistance to allow mass transfer between two phases.

Hardly any solvent will satisfactorily meet all the above criteria. Choosing a solvent is again a matter of striking a balance between properties and cost of solvent and equipment and operating costs and ease of operation of the other.

Construction of conjugate line using tie line data

Only a few experimental tie line data for a ternary system are generally available. From the available tie line data, conjugate line is drawn. A horizontal line is drawn through the end G of the tie line GH. A vertical line is drawn through the end H. These two lines meet at K.The locus of the point K is called the "conjugate line".

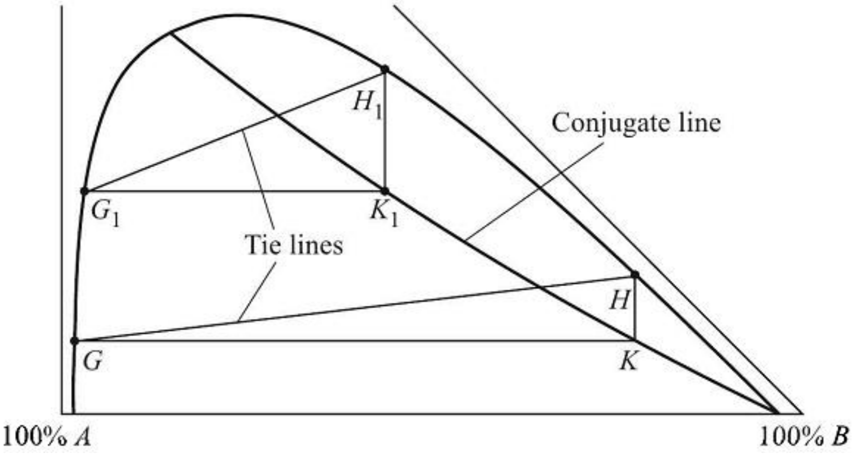


Figure 9

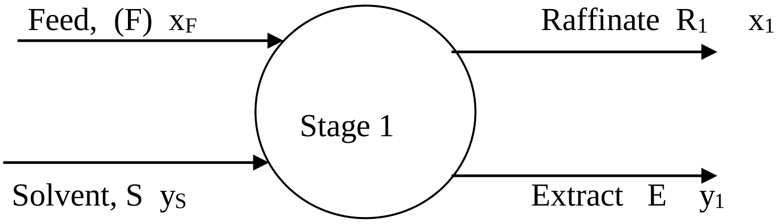
Equipment and flow-sheets:

1) Stage-wise contact operation

a) Single stage extraction
b) Multistage cross-current extraction

2) Differential (continuous contact) operation

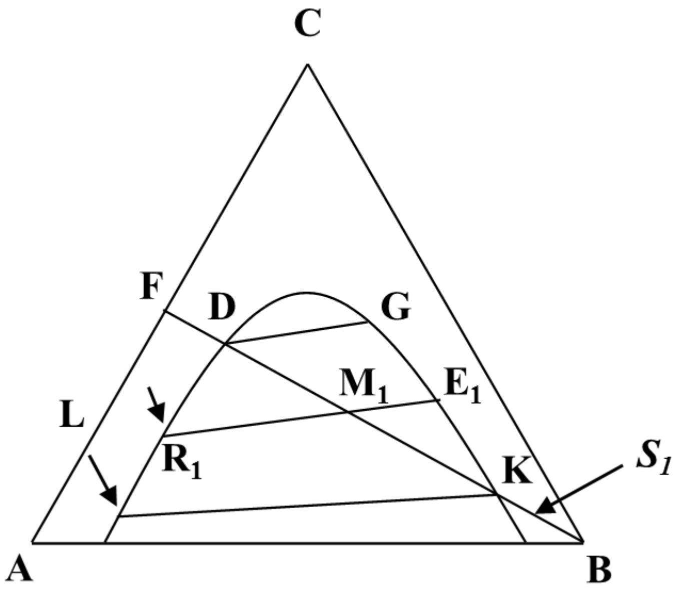
Single stage extraction



Total material balance, $F + S_1 = E_1 + R_1 = M_1 \longrightarrow$ Mixture $\dashrightarrow$ (1)

Solute balance $Fx_F + S_1y_S = E_1y_1 + R_1x_1 = M_1x_{M1}$

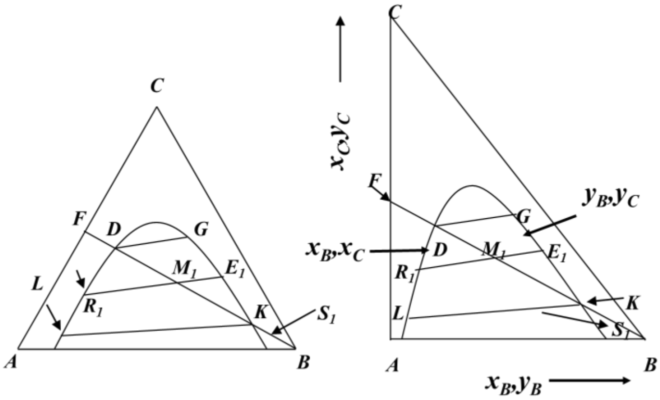
⇨ $X_{M1} = (Fx_F + S_1y_S)/(F + S_1)$ $\dashrightarrow$ (2)
$Fx_F + S_1y_S = (F + S_1)x_{M1}$
⇨ $F(x_F - x_{M1}) = S_1(x_{M1} - y_S)$
⇨ $F/S_1 = (x_{M1} - y_S)/(x_F - x_{M1})$ $\dashrightarrow$ (3)
Again, $E_1y_1 + R_1x_1 = M_1x_{M1} = (E_1 + R_1)x_{M1}$
⇨ $E_1(y_1 - x_{M1}) = R_1(x_{M1} - x_1)$
(4)
⇨ $E_1/R_1 = (x_{M1} - x_1)/(y_1 - x_{M1})$ $\dashrightarrow$ (4)



Equation (4) indicates that point M lies on the line joining the points E_1 and R_1. The minimum amount of solvent is found by locating M_1 at D. The amount of extract at point

G. Maximum amount of solvent is found by locating M_1 at K. Point L represents the raffinate with lowest possible C conc.

Steps of graphical procedure:



1) Draw the ternary equilibrium curve on the equilateral triangular diagram (or any other suitable diagram). Locate points F and S_1.

2) Calculate x_{M1} from material balance equation and locate point M_1 on the line FS_1.

3) Draw the tie line E_1R_1 through the point M_1. The terminals of the tie line give the extract and raffinate concentrations y_1 and x_1. The amount of extract and raffinate phases (E_1 and R_1) and the percentage of the solute separated from the feed can now be calculated from the equations:

$F + S_1 = M_1 = E_1 + R_1$; $Fx_F + S_1y_S = M_1x_{M1} = E_1y_1 + R_1x_1$ and

$E_1/R_1 = (x_{M1}- x_1)/(y_1- x_{M1})$.

If a required percentage separation of solute is specified, the necessary solvent rate can be calculated. For that ,we have to calculate R_1 and x_1. As x_1 is known, y_1 is calculated from equilibrium plot. E_1 will be expressed in terms of S_1 as $E_1=F+S_1-R_1$. This will involve trial and error method.

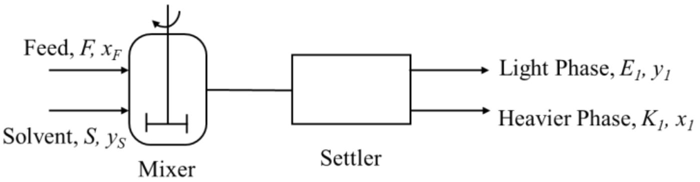
Problem 2: 1000kg of an aqueous solution containing 50% acetone is contacted with 800kg of chloro-benzene containing 0.5 mass% acetone in a mixer settler unit, followed by separation of the extract and the raffinate phases.

(a) Determine the composition of extract and raffinate phases and the fraction of acetone extracted.

(b) Calculate the amount of solvent required if 90% of acetone is to be removed. Equilibrium and tie line data are given below.

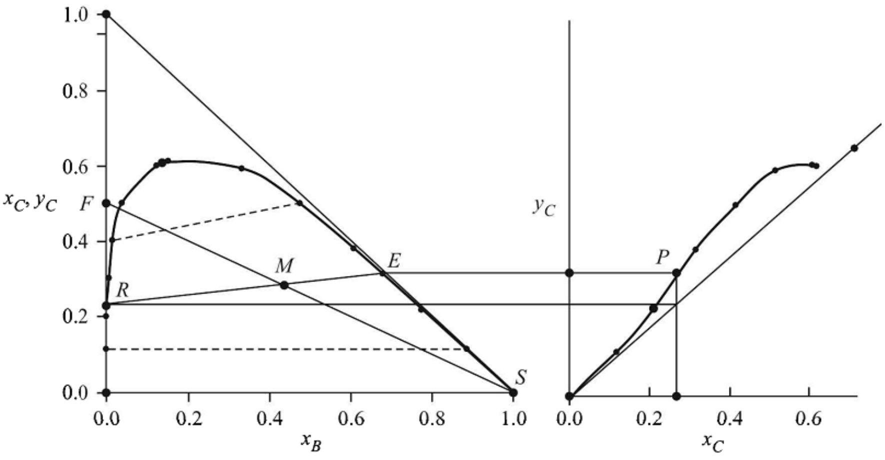
Aqueous phase (Raffinate)			Organic phase (Extract)		
Water (x_A)	**Chlorobenzene (x_B)**	**Acetone (x_C)**	**Water (y_A)**	**Chlorobenzene (y_B)**	**Acetone (y_C)**
0.9989	0.0011	0	0.0018	0.9982	0
0.8979	0.0021	0.1	0.0049	0.8872	0.1079
0.7969	0.0031	0.2	0.0079	0.7698	0.2223
0.6942	0.0058	0.3	0.0172	0.608	0.3748
0.5864	0.0136	0.4	0.0305	0.4751	0.4944
0.4628	0.0372	0.5	0.0724	0.3357	0.5919
0.2741	0.1259	0.6	0.2285	0.1508	0.6107
0.2566	0.1376	0.6058	0.2566	0.1376	0.6058

Solution:



Given:
Mass of feed (F) = 1000kg, $x_F = 0.5$
Mass of solvent S_1 = 800kg, $y_S = 0.005$
$M_1 = F + S_1 = 1000 + 800 = 1800$kg
$X_{M1} = (Fx_F + S_1y_S)/(F + S_1) = (1000\times0.5 + 800\times0.005)/(1800) = 0.28$

The equilibrium data is plotted using right triangular co-ordinate
Point F ($x_B = 0$, $x_C = 0.5$)
Point S_1(x_B or $y_B = 0.995$, $y_C = 0.005$)
Point P corresponds to the tie line R_1E_1



(a) (b)

From the figure:-

Solute concentration in the raffinate x_1 =0.236

Solute concentration in the extract y_1 = 0.302

$E_1/R_1 = (x_{M1} – x_1)/(y_1 – x_{M1}) = (0.28 – 0.236)/(0.302 – 0.28)$

And $E_1 + R_1 = 1800$

- E_1 = 1200kg
- R_1 = 600kg
- Mass of acetone leaving with extract = E_1y_1 = 1200×0.302 = 362.4 kg

Mass of acetone in the feed = 1000×0.5 = 500kg

Acetone entering with the solvent = 800×0.005 =4kg

Net amount of acetone transported to the extract stream = 362.4 – 4 = 358.4 kg

Fraction of acetone removed by extraction = 358.4/ 500 = 71.68%

b) If 90% of acetone is removed, then acetone remaining in the aqueous phase = 500×0.1 = 50kg.

The mutual solubility of water and chlorobenzene is negligible at this low concentration of acetone. So raffinate (aq. Phase) is almost free from chlorobenzene.

- R_1 = (50 + 500)kg = 550kg
- X_1 = 50/ 550 =0.091
- Y_1 = 0.105 (from fig.) R_1 = 550kg
- $E_1 =1000 – S_1 – 550 = 450 + S_1$

$Fx_F + S_1y_S = E_1y_1 + R_1x_1$

- 1000×0.5 + S1×0.005=(450 + S_1)× 0.105 + 550× 0.091
- S_1 = 4027.5kg

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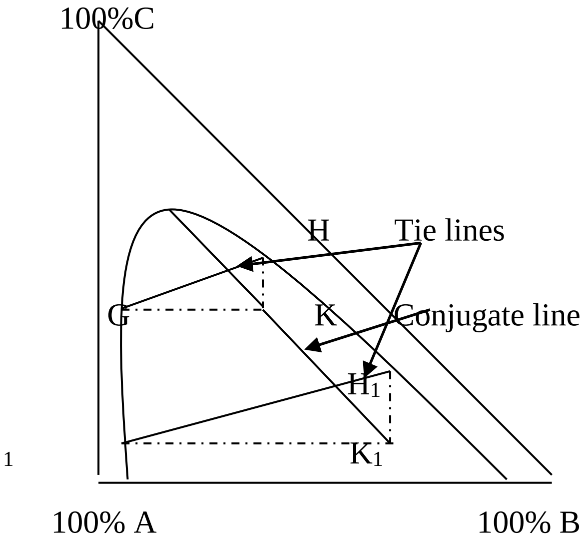

Construction of conjugate line using tie line data

So thank you very much, in the next class actually we will be doing this design calculation for multistage extraction.