LIQUID-LIQUID EQUILIBRIUM AND EXTRACTION USING MATHEMATICA®

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Abstract

In the present paper, we show a new approach, based on the utilization of *Mathematica*®, to solve liquid-liquid extraction problems. Since liquid-liquid equilibrium data are primordial for the design of extraction columns, we start with the calculation of such data for a multi-component mixture using the NRTL model. We will consider a ternary mixture of benzene - ethanol - water at 25°C. The built-in *Mathematica*® function, *FindRoot*, is used to solve a system of nonlinear algebraic equations traducing the equilibrium relation between the two liquid phases. We also study the separation[1] of acetic acid from water using isopropyl ether for each of the following cases: single-feed countercurrent extractor and two-feed extraction column. We use the graphical method derived by Hunter and Nash[2] and later by Kinney[3] to obtain for both cases the number of equilibrium stages required to achieve a particular raffinate specification. Finally, we use the McCabe-Thiele diagram to obtain the same value of the number of equilibrium stages. The notebooks are available from the author upon request or at Wolfram Research[4].

Key words: Liquid-liquid extraction, tie-lines, NRTL model, Hunter-Nash diagram, McCabe-Thiele method

Liquid-Liquid Equilibrium Diagram of A Ternary Mixture

We present in this section, the computation of equilibrium data for the ternary system: benzene - ethanol - water at a temperature of 25°C. Application of such equilibrium diagram include heterogeneous azeotropic distillation to obtain anhydrous ethanol using benzene as an entrainer (e.g. the three column Kubierschky system). This ternary system is of a Type I with a plait point separating the raffinate phase and the extract phase. In order to take into account liquid demixtion, we will use the liquid phase activity coefficients from the NRTL model[5] given by equation (1):

$$\ln\gamma_i = \frac{\sum_{j=1}^{C}\tau_{ji}G_{ji}x_j}{\sum_{k=1}^{C}G_{ki}x_k} + \sum_{j=1}^{C}\left[\frac{x_j G_{ij}}{\sum_{k=1}^{C}G_{kj}x_k}\left(\tau_{ij} - \frac{\sum_{k=1}^{C}\tau_{kj}G_{kj}x_k}{\sum_{k=1}^{C}G_{kj}x_k}\right)\right] \quad (1)$$

where x_i is the mole fraction of a component and G_{ij} and τ_{ij} are written as follows,

$$G_{ji} = \exp\left(-\alpha_{ji}\tau_{ji}\right) \quad \tau_{ij} = \frac{(g_{ij} - g_{jj})}{RT} \quad (2)$$

The energy parameters (expressed in kcal/kmol), g_{ij}, and the nonrandomness parameters, α_{ij}, are given in Tables 1 and 2.

g_{ij}	Benzene	Ethanol	Water
Benzene	0	334.1524	3719.395
Ethanol	991.5067	0	1332.312
Water	4843.376	-109.6339	0

Table 1 - Energy parameters.

α_{ij}	Benzene	Ethanol	Water
Benzene	0	0.291099	0.20
Ethanol	0.291099	0	0.303099
Water	0.20	0.303099	0

Table 2 - Nonrandomness parameters.

The condition of equilibrium states that the activities in the two liquid phases must be equal:

$$x_i^1 \gamma_i^1 = x_i^2 \gamma_i^2 \quad i = 1,2,3 \tag{3}$$

We also have additional relations such as the summation rules and material balances:

$$\sum_{i=1}^{i=3} x_i^1 = 1 \quad and \quad \sum_{i=1}^{i=3} x_i^2 = 1 \tag{4}$$

$$L^1 + L^2 = 1 \quad and \quad L^1 x_i^1 + L^2 x_i^2 = X_i \quad i = 1,2 \tag{5}$$

Equations 1-5 can be solved simultaneously using the built-in *Mathematica*® function, *FindRoot*, in order to get the eight unknown, x_i^1, x_i^2, L^1 *and* L^2, which are the mole fractions in both liquid phase for the three components and the total number of moles in the two liquid phase in equilibrium. If we solve this system of equations for different values of X_1 *and* X_2, we get Figure 1. Tie lines are obtained by joining with lines the equilibrium points, the extract and raffinate curves are also plotted. The system considered in this study is a Type I where the a plait point is marked as a bold dot in the figure.

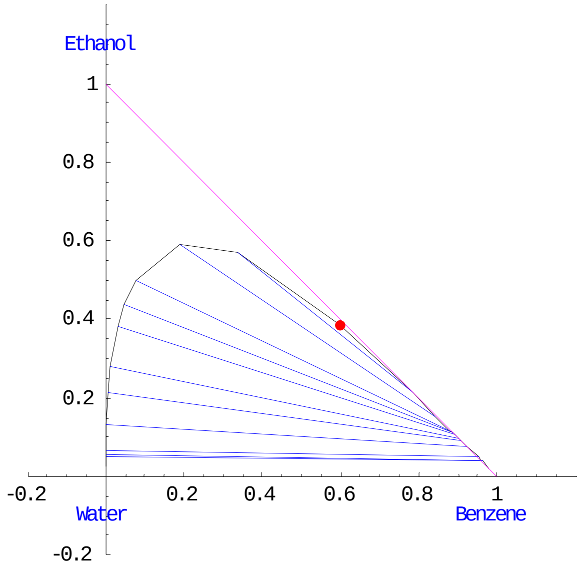

Figure 1 - Liquid-liquid equilibrium diagram for a ternary system.

Extraction of Acetic Acid from Water Using Isopropyl Ether

We will now study the separation of acetic acid from water using isopropyl ether as a solvent. This separation is usually difficult to realize with distillation due to the presence of a severe tangent pinch at high compositions of water which prevent the distillate from being acid-free. A graphical solution performed by hand calculation has been presented by Wankat[1]. We will show how one can use *Mathematica*® to solve this problem more easily and accurately using the graphical approach of Hunter and Nash[2] as well as the McCabe-Thiele diagram. Equilibrium data, at 1 atm and 25°C, are given by Wankat[1], they can be used to plot the following diagram where the tie lines has been drawn (see Figure 2). Note that the conjugate line can be easily constructed using the equilibrium points.

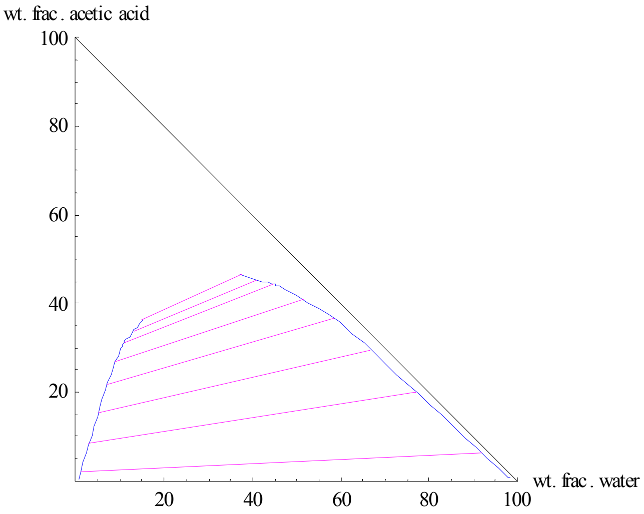

Figure 2 - Equilibrium data for the ternary system.

1-Single feed countercurrent extractor

The feed is 1000 kg/hr of a solution composed of 35 wt % acetic acid and 65 wt % water. The solvent used to perform the extraction is pure isopropyl ether with a flow rate equal to 1475 kg/hr. We require that the raffinate composition in acid do not exceed 10 wt %. First, we locate the mixing point and the difference point. Then, we step off stages using alternatively the tie lines and the operating lines until we reach a raffinate composition lower than 10 wt %. The method is illustrated in Figure 3. We find that 5.35 equilibrium stages are required to achieved 10 wt % of acid in the raffinate.

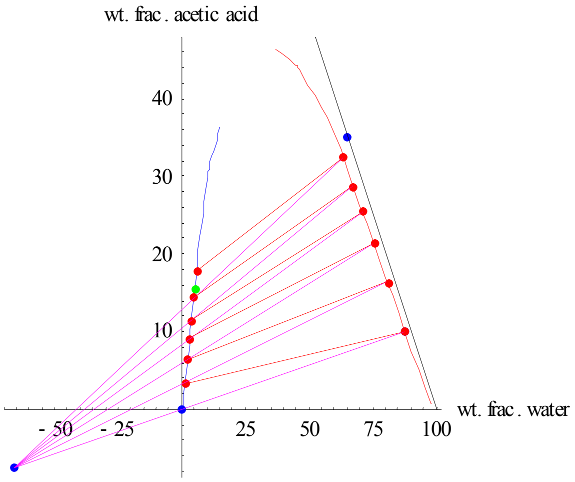

Figure 3 - Hunter and Nash diagram for the single feed case.

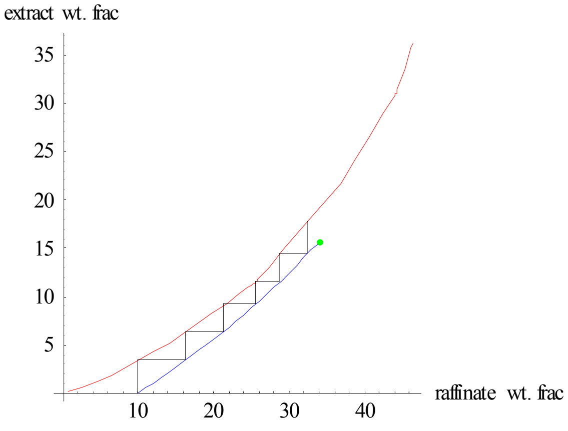

Figure 4 - McCabe-Thiele diagram for the single feed case.

Using the triangular diagram (see Figure 3) and the procedure described by Wankat[1], we can get the McCabe-Thiele diagram shown in Figure 4. We draw steps between the equilibrium and operating lines to get the total number of equilibrium stages which will achieve the raffinate specification. We find that both methods are in agreement.

2- Two-feed extraction system

Pure isopropyl ether with a flow rate of 1800 kg/hr is used to extract acetic acid from water. Two feeds composed of water and acid are used in this case; the first feed rate and acid composition are, 600 kg/hr and 35 wt. % respectively, while the second feed has the following characteristics: feed flow rate of 400 kg/hr and weight fraction of acid equal to 20 wt. %. As in the previous case, we would like to achieve a raffinate purity of 10 wt. % in acetic acid. We find the mixing point and the two difference points, Δ_1 *and* Δ_2 ,as described by Wankat[1] using *Mathematica*$^{®}$. We start by stepping off the stages using the first difference point until a tie line intersect the line joining the two difference points and the second feed point F_2. Finally, we step off the stages using the second difference point until we reach the raffinate specifications. Figure 5, obtained with *Mathematica*$^{®}$, shows the entire graphical procedure. We find a total of 2.89 stages as well as the location of the optimum feed stage which for this particular case turns out to be stage number 2.

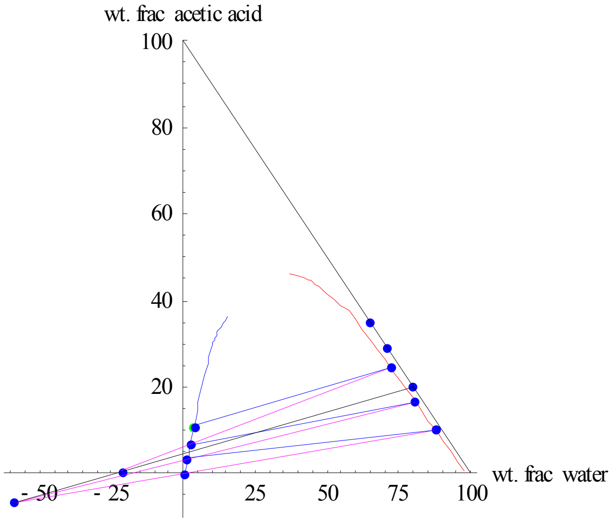

Figure 5 - Hunter and Nash diagram for the two feed case.

Conclusion

In this study, we showed how simple *Mathematica*® commands can be used to solve problems that required in the past tedious numerical and graphical techniques. We present the computation of the equilibrium diagram of a the ternary mixture (benzene - ethanol - water). We also solve two problems proposed by Professor Wankat[1]. These problems concern the extraction of acetic acid from water using isopropyl ether. The graphical method, derived by Hunter and Nash, is used to obtain the number of equilibrium stages for a specific raffinate purity. Finally, the McCabe-Thiele method is employed to give the same result. These classic problems are junior and senior level study material at the National Institute of Applied Sciences in Tunis. The students excel in these type of problems despite the fact that they do not have prior knowledge of *Mathematica*®.

References

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Biographical Information

Dr. Housam Binous is a full time faculty member at the National Institute of Applied Sciences and Technology in Tunis. He earned a Diplôme d'ingénieur in Biotechnology from the Ecole des Mines de Paris and a Ph.D. in Chemical Engineering from the University of California at Davis. His research interests include the applications of computers in Chemical Engineering.