

# RESIDUE CURVE MAP CALCULATION OF A TERNARY MIXTURE

Housam Binous\*, Aïda Wakad and Saïda Ben Achour  
National Institute of Applied Sciences and Technology  
BP 676 Centre Urbain Nord, 1080 Tunis, Tunisia  
\*corresponding author: [binoushousam@yahoo.com](mailto:binoushousam@yahoo.com)

## Abstract

In the present paper, the residue curve map (RMC) for the ternary system chloroform - methanol - acetone is computed with the help of *Mathematica*<sup>®</sup> using two methods. The first method uses the built-in function of *Mathematica*<sup>®</sup>, FindRoot, to get the vapor mole fractions, and Euler's method to integrate the governing differential equations. The second method solves the differential algebraic equations (DAEs) using the built-in function of *Mathematica*<sup>®</sup>, NDSolve. In addition, we show how one can find all binary and ternary azeotropes of this mixture using FindRoot. These pedagogic problems are currently being used to describe simple methods to solve DAEs in the applied math course taught at the Chemical Engineering Department of the National Institute of Applied Sciences and Technology in Tunis. They serve also to introduce students to the conceptual design of distillation columns in the process design course.

**Keywords:** Residue curve map, Differential algebraic equation, Wilson model, ternary systems, azeotropes

## Introduction

Residue curve maps are very useful for the understanding of the behavior of ternary mixtures and the design of distillation systems. In addition, computing residue curve maps allows one to find azeotropes as stable nodes, unstable nodes or saddle points.

The governing equation[1] that links the liquid mole fraction in the boiler  $x_i$  to the corresponding vapor mole fraction  $y_i$  can be derived from the Rayleigh equation, and has the following final form:

$$\frac{dx_i}{d\xi} = x_i - y_i \quad (1)$$

where  $\xi$  is a warped time variable. From equation (1), it appears that pure components and azeotropes are extreme points in the residue curve map since they satisfy the following equation:

$$x_i = y_i \quad (2)$$

If we assume that the deviation from ideal behavior is only in the liquid phase (low total pressure), we can relate the liquid and vapor mole fractions using the modified Raoult's law,

$$Py_i = x_i P_i^{sat} \gamma_i \quad (3)$$

where  $\gamma_i$ , the activity coefficient obtained using Wilson's model[2] for multi-component mixtures,

$$\ln \gamma_k = -\ln \left( \sum_{j=1}^m x_j A_{kj} \right) + 1 - \sum_{i=1}^m \frac{x_i A_{ik}}{\sum_{j=1}^m x_j A_{ij}} \quad (4)$$

In equation (4),  $A_{ij}$  is the binary interaction parameter which depends on the molar volumes ( $v_i$  and  $v_j$ ) and the energy terms  $\lambda_{ii}$  and  $\lambda_{ij}$ ,

$$A_{ij} \equiv \frac{v_j}{v_i} \exp \left( -\frac{\lambda_{ij} - \lambda_{ii}}{RT} \right) \quad (5)$$

The vapor pressure  $P_i^{sat}$  is obtained using Antoine's equation,

$$\ln P_i^{sat} = A_i - \frac{B_i}{C_i + T} \quad (6)$$

For the ternary system acetone (1) - chloroform (2) - methanol (3), Antoine's constants are given in Table (1).

Values of molar volumes[3] (expressed in  $\text{cm}^3/\text{mol}$ ) and energy parameters[3] (expressed in kcal/kmol) are:

$$\begin{aligned} \lambda_{12} &= 116.1171 ; & \lambda_{21} &= -506.8519 ; \\ \lambda_{13} &= -114.4047 ; & \lambda_{31} &= 545.2942 ; \\ \lambda_{23} &= -361.7944 ; & \lambda_{32} &= 1694.0241 ; \\ v_1 &= 74.05 ; & v_2 &= 80.67 ; & \text{and } v_3 &= 40.73 . \end{aligned}$$

### Computing the azeotropes of the ternary system

The FindRoot command is used to solve the system of nonlinear algebraic equations that defines the azeotropes. To get all three binary azeotropes as well as the ternary azeotrope, the initial guess of the FindRoot function must be changed by the user.

```
FindRoot[{Y1<X1,Y2<X2,
P==X1*PS1*GAM1+X2*PS2*GAM2+X3*PS3*GAM3},
{X1,0.3},{X2,0.4},{T,40}]
```

	A	B	C
Acetone (1)	7.11714	1210.595	229.664
Chloroform (2)	6.95465	1170.966	226.232
Methanol (3)	8.08097	1582.271	239.726

Table 1 - Antoine's constants[3].

	$x_1$	$x_2$	$x_3$	$T_{eb} (^{\circ}\text{C})$
Az <sub>1</sub>	0.3231	0.2303	0,4465	57.3763
Az <sub>2</sub>	0	0.6547	0,3372	53.896
Az <sub>3</sub>	0.7895	0	0,2104	55.3768
Az <sub>4</sub>	0.3372	0.6627	0	64.5366

Tableau 2: Azeotropes of the ternary system.

The composition and boiling temperature of the different azeotropes is given in Table (2). Total pressure was taken equal to 760 mmHg. Az<sub>1</sub> is the ternary azeotrope and all other are binary azeotropes.

### RCMs using FindRoot and Euler's method

The following *Mathematica*<sup>®</sup> command computes the residue curve from an initial starting point using a while loop where FindRoot and Euler's method are invoked:

```
While[i<200,{T=FindRoot[P == Evaluate[x1[i]
PS1[i] GAM1[i]+x2[i] PS2[i] GAM2[i]+x3[i] PS3[i]
GAM3[i]],{T,100}][[1,2]],
y1[i]=x1[i] PS1[i] GAM1[i]/P,y2[i]=x2[i] PS2[i]
GAM2[i]/P,
y3[i]=x3[i] PS3[i] GAM3[i]/P,x1[i+1]=x1[i]-h (x1[i]-
y1[i]),
x2[i+1]=x2[i]-h (x2[i]-y2[i]),x3[i+1]=x3[i]-h (x3[i]-
y3[i]),i++];
```

FindRoot allows one to compute the bubble point using the liquid mole fractions, the vapor mole fractions are then calculated using modified Raoult's law. Finally, Euler's method enables one to obtain the next point in the residue curve.

If all residue curves, starting from different initial points, are plotted, one obtains the RCM shown in Figure 1 and obtained with *Mathematica*<sup>®</sup>. We clearly see that the azeotropes and pure components are extreme points in this RCM.

### RCMs using NDSolve to solve a DAE

The following *Mathematica*<sup>®</sup> command computes the residue curve from an initial starting point using NDSolve.

```
sol1=NDSolve[{D[x1[t],{t,1}]=y1[t]-x1[t],
D[x2[t],{t,1}]=y2[t]-x2[t],D[x3[t],{t,1}]=y3[t]-
x3[t],
D[T[t],{t,1}]=10^7(x1[t]PS1[t]GAM1[t]+
x2[t]PS2[t]GAM2[t]+x3[t]PS3[t]GAM3[t]-P),
T[0]=57.5898,x1[0]=0.2,x2[0]=0.2,x3[0]=
0.6},{x1,x2,x3,T},{t,0,40},
AccuracyGoal->Infinity,MaxSteps->Infinity,
StartingStepSize->0.0001,MaxStepSize->0.0001}
```

The first three equations are the differential governing equations (see equation 1) written for all three components (acetone, chloroform and methanol; respectively) while the fourth equation is the algebraic equation giving the bubble point temperature. Since  $\frac{dT}{dt}$  is finite

and  $10^7$  is very large, we must have the following algebraic relation:

$$P = x_1 P_1^{sat} \gamma_1 + x_2 P_2^{sat} \gamma_2 + x_3 P_3^{sat} \gamma_3 \quad (7)$$

The second approach gives the same result as shown in Figure 1. The first method presented requires more computational time.

### Conclusions

*Mathematica*<sup>®</sup> graphical and numerical features can be very helpful in computing RCM's for different ternary mixtures using all

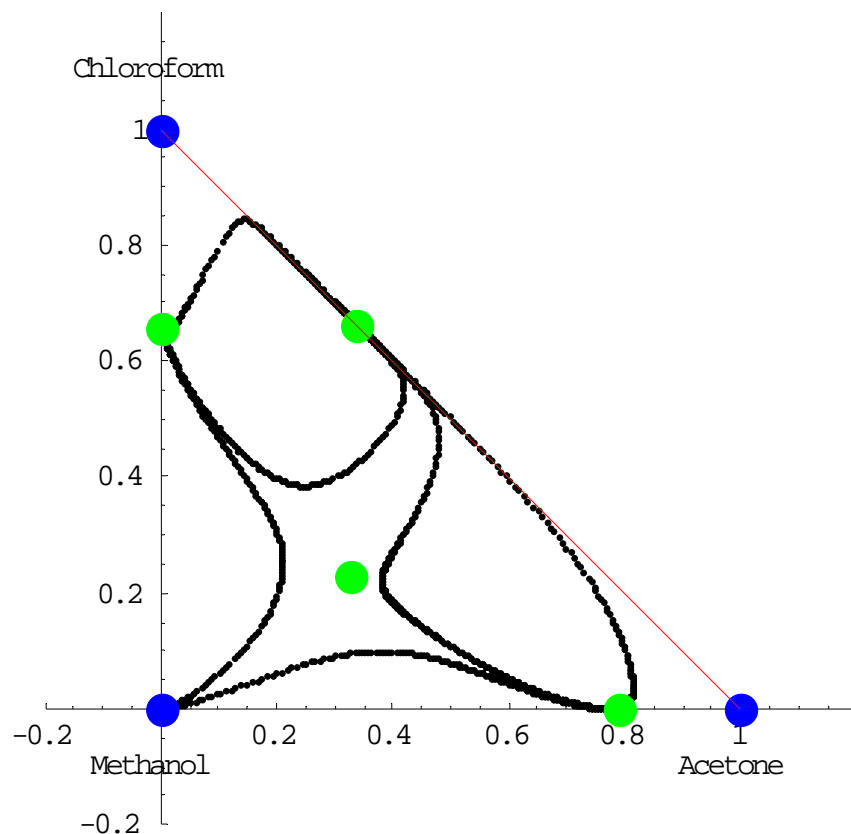


Figure 1: RCM of the ternary mixture.

kind of thermodynamic models and conditions. In fact, one can easily extend this work to other thermodynamic models such as NRTL, to other ternary mixtures or to higher total pressures where deviation from ideality in the gas phase must be taken into account. The author will show in a future paper that similar ideas can be used to compute RCMs when reactions between components are taking place such as in the case of the methyl acetate and isopropyl acetate chemistries. These classic problems are junior and senior level study material at the National Institute of Applied Sciences and Technology in Tunis. The students excel in these types of problems despite the fact that they do not have prior knowledge of *Mathematica*<sup>®</sup>. The notebooks are available from the corresponding author upon request or at Wolfram Research.[4] The authors have also computed the same residue curve map using Matlab and Simulink.[5]

## 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 from the Ecole des Mines de Paris and a Ph.D. from the University of California at Davis.

Aïda Wakad and Saïda Ben Achour are students in the Masters program at the National Institute of Applied Sciences and Technology in Tunis. They performed the RCM calculations, as a partial requirement to obtain their engineering degree, under the supervision of Dr. Housam Binous.

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