Computer Aided Identification of Acetone and Chloroform Mixture Behavior

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Abstract

Mixtures are either ideal or non ideal. Ideal mixtures follow the Raoult's rule while the non ideal ones show an azeotropic behavior. The ratio of the compounds, in an azeotropic mixture, is exactly the same in both the vapor form of the mixture as in the liquid phase. A method to predict mixtures' behavior is to plot their boiling point diagram. Aspen software provides us a reasonable tool to graph the mixtures' boiling point diagram. This article illustrates how to use Aspen software in order to predict acetone and chloroform's behavior. As the resulting graphs show, the binary mixture of acetone- chloroform is a minimum pressure azeotrope. The Aspen modeling results are in good agreement with the experimental data.

Keywords: Non ideal Mixture, Azeotrope, Acetone, Chloroform, Aspen Software

1. Introduction

Empirically it has been found that in very dilute solutions the vapor pressure of solvent (major component) is proportional to its mole fraction (X). The proportionality constant is the vapor pressure (p_o) of the pure solvent. This rule is called Raoult's law:

$$p_{solvent} = p^o_{solvent} . X_{solvent} \quad \text{for } X_{solvent} = 1 \qquad (1)$$

For a truly ideal solution, this law should apply over the entire range of compositions. If the P-Y (bubble point curve) lies below or above a linear P-Y relation, the system exhibits deviations from Raoult's Law (ideal-solution behavior) and shows azeotrpic behavior.

At low to moderate pressure, with the assumption of ideal-gas model for the vapor phase, the vapor-liquid phase equilibrium (VLE) of many mixture can be adequately describe by the following Modified Raoult's Law: (3)

$$y_i P = x_i \gamma_i P_i^{sat} \quad \text{for } i = 1, \ldots, c \qquad (1)$$

Where:

y_i	=	mole fraction of component i in vapor phase
x_i	=	mole fraction of component i in liquid phase
P	=	system pressure
P^{sat}	=	vapor pressure of component i
γ_i	=	liquid-phase activity coefficient of component i

When $\gamma_i = 1$, the mixture is said to be ideal Equation 1 simplifies to Raoult's Law. Nonideal mixtures can exhibit either positive ($\gamma_i > 1$) or negative deviations ($\gamma_i < 1$) from Raoult's Law.

The word azeotrope comes from the Greek "zein tropos", or "constant boiling". An azeotrope is said to be positive if the constant boiling point is at a temperature maximum (or at a pressure minimum), and negative when the boiling point is at a temperature minimum (or at a pressure maximum). Separation of one component from another by fractional distillation is impossible at this composition because the vapor and liquid phase have the same composition.

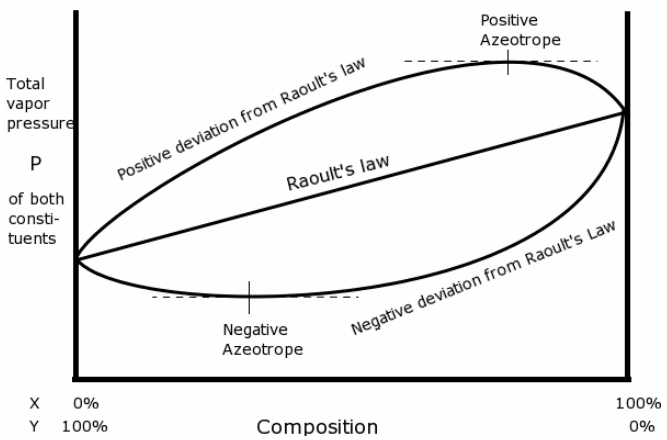


Figure 1- Total vapor pressure diagram of a mixture of two solvents

At these minimum and maximum boiling azeotrope, the liquid phase and its equilibrium vapor phase have the same composition, i.e.,

$$x_i = y_i \qquad \text{for } i = 1, \ldots, c \qquad (4)$$

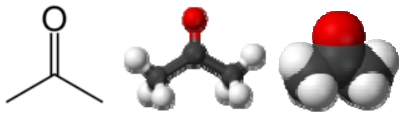
[1], [2], [3], [4], [5], [6]

2. Materials

2.1. Acetone

The chemical compound acetone (also known as propanone, dimethyl ketone, 2-propanone, propan-2-one and β-ketopropane) is the simplest representative of the ketones. Acetone is a colorless, mobile, flammable liquid with a freezing point of −95.4 °C and boiling point of

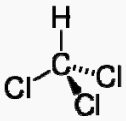
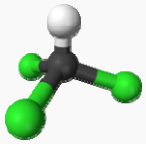
56.53 °C. It has a relative density of 0.819 (at 0 °C). It is readily soluble in water, ethanol, ether, etc., and itself serves as an important solvent.

	
Systematic name	Propan-2-one
Other names	β-ketopropane Dimethyl ketone,
Molecular formula	CH_3COCH_3
Molar mass	58.09 g/mol
Appearance	Colorless liquid

[3], [7]

2.2. Chloroform

Chloroform, also known as trichloromethane and methyl trichloride, is a chemical compound with formula $CHCl_3$. It does not undergo combustion in air, although it will burn when mixed with more flammable substances. It is a member of a group of compounds known as trihalomethanes. Chloroform has myriad uses as a reagent and a solvent. It is also considered an environmental hazard.

	
IUPAC name	Chloroform
Other names	Trichloromethane, Formyl trichloride, Methane trichloride, Methyl trichloride, Methenyl trichloride, TCM, Freon 20, R-20, UN 1888
Molecular formula	$CHCl_3$

Molar mass	119.38 g/mol
Appearance	Colorless liquid
Density	1.48 g/cm³, liquid
Boiling point	61.2 °C

[3], [8]

2.3. Acetone- Chloroform Mixture

Neat acetone and chloroform do not exhibit hydrogen bonding. When mixed, it is hypothesized that chloroform is able to form hydrogen-bonded complexes with acetone which result is a minimum pressure azeotrope. [9]

3. Methods

There are 2 ways to reach the azeotopic data of the mixtures:

- Using the relevant books (such as series of books issued by DECHEMA / Gmehling and also CRC handbook of chemistry)
- Applying computer modeling [10]

If the mixture data is not found in the books or if we don't have access to the books the best way to solve our problem is to use appropriate software such as aspen to graph the bubble point curve.
To use the Aspen Software we have to define a stream which will be sent to a flash drum. The properties of the stream and flash drum will be designated as below:

- Stream properties (labeled as Feed): T=50°C, P=1 bar, Flow rate: 200 lbmole/hr
- Flash drum properties: T=50°C

Feed is consisted of Acetone (1) and Chloroform (2). By using Model Analysis tool, the mole percent of acetone in the vapor resulting from the flashing will be calculated.
The pressure at which the feed would flash (will result in the generation of both liquid and vapor phases) depends on the mole percent of the Acetone. Aspen has been run for several times while in each time various feed mole percent compositions has been designated.

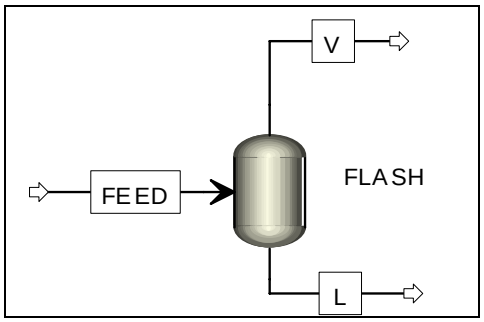


Figure 2- Process Flow Diagram

The selected equation of state is UNIQUAC. The binary coefficients are printed in Dechema handbook (Goral M. Kolasinska G. Oracz P.(1985)) which are:

A12=-295.3605 , A21=109.7564

The results are shown in tables 1 and 2.

Table 1- Y1 while feed has various X1 (A12=-295.3605 & A21=109.7564)

X1 / P(mmHg)	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
400	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
405	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
410	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
415	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
420	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
425	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
430	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
435	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
440	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
445	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
450	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
455	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
460	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
465	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.549421
470	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	
475	1	0.99	0.98	0.95	0.9	0.8	0.7	0.629614	
480	1	0.99	0.98	0.95	0.9	0.8	0.7	0.660656	
485	1	0.99	0.98	0.95	0.9	0.8	0.7		
490	1	0.99	0.98	0.95	0.9	0.8	0.712658		
495	1	0.99	0.98	0.95	0.9	0.8	0.735013		
500	1	0.99	0.98	0.95	0.9	0.8	0.755516		
505	1	0.99	0.98	0.95	0.9	0.8	0.774448		
510	1	0.99	0.98	0.95	0.9	0.8	0.792025		
515	1	0.99	0.98	0.95	0.9	0.808417			
520	1	0.99	0.98	0.95	0.9	0.823718			
525	1	0.99	0.98	0.95	0.9	0.838175			
530	1	0.99	0.98	0.95	0.9	0.85173			
535	1	0.99	0.98	0.95	0.9	0.864541			
540	1	0.99	0.98	0.95	0.9	0.876641			
545	1	0.99	0.98	0.95	0.9				
550	1	0.99	0.98	0.95	0.9				
555	1	0.99	0.98	0.95	0.909302				
560	1	0.99	0.98	0.95	0.919129				
565	1	0.99	0.98	0.95	0.928484				
570	1	0.99	0.98	0.95	0.937401		*		
575	1	0.99	0.98	0.95	0.945919				
580	1	0.99	0.98	0.954046					
585	1	0.99	0.98	0.96181					
590	1	0.99	0.98	0.969234					
595	1	0.99	0.98	0.976338					

600	1	0.99	0.983147						
605	1	0.99	0.98966						
610	1								
615									

* All the empty cells mean that the feed is still liquid at that specifies pressure.

Rest of table 1:

X1 / P(mmHg)	0.4	0.3	0.25	0.2	0.1	0.05	0.02
400	0.4	0.3	0.25	0.2	0.1	0.05	0.02
405	0.4	0.3	0.25	0.2	0.1	0.05	0.02
410	0.4	0.3	0.25	0.2	0.1	0.05	0.02
415	0.4	0.3	0.25	0.2	0.1	0.05	0.02
420	0.4	0.3	0.25	0.2	0.1	0.05	0.02
425	0.4	0.3	0.25	0.2	0.1	0.05	0.02
430	0.4	0.3	0.25	0.2	0.1	0.05	0.02
435	0.4	0.3	0.25	0.2	0.1	0.05	0.02
440	0.4	0.3	0.25	0.2	0.1	0.05	0.02
445	0.4	0.3	0.25	0.2	0.1	0.05	0.02
450	0.4	0.3	0.25	0.2	0.1	0.05	0.02
455		0.3	0.25	0.2	0.1	0.05	0.02
460			0.25	0.2	0.1	0.05	0.02
465				0.199139	0.1	0.05	0.02
470				0.16266	0.1	0.05	0.02
475					0.1	0.05	0.02
480					0.1	0.05	0.02
485					0.090074	0.05	0.02
490					0.072559	0.05	0.02
495						0.05	0.02
500						0.05	0.02
505						0.031406	0.02
510							0.02
515							0.010667
520							

Table 2- P-Y1 calculated data (A12=-295.3605 & A21=109.7564)

P (mmHg)	Y1	P (mmHg)	Y1	P (mmHg)	Y1	P (mmHg)	Y1
520	0	460	0.25	510	0.792025	565	0.928484
515	0.010667	455	0.4	515	0.808417	570	0.937401
505	0.031406	465	0.549421	520	0.823718	575	0.945919

500	0.043539	475	0.629614	525	0.838175	580	0.954046
495	0.049603	480	0.660656	530	0.85173	585	0.96181
490	0.072559	490	0.712658	535	0.864541	590	0.969234
485	0.090074	495	0.735013	540	0.876641	595	0.976338
470	0.16266	500	0.755516	555	0.909302	600	0.983147
465	0.199139	505	0.774448	560	0.919129	605	0.98966
						610	1

By applying the Binary Coefficients dedicated by Ionescu Gh.,Onu A., Nagacevschi V. (1989) printed in Dechema handbook:

A12=125.1797 , A21=-262.0684

we ran Aspen for several times. The temperature is constant and by model Analysis Tool we designate various pressures in flash drum. For various X1 of the feed, we run Aspen. The boiling pressure of the feed depends on its Acetone (1) mole percent. Finally we put all the results together to have the P-Y1 curve. The results are shown in tables 3 and 4.

Table 3-Y1 while feed has various X1 (A12=125.1797 & A21=-262.0684)

X1 / P(mmHg)	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
400	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
405	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
410	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
415	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
420	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
425	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
430	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
435	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
440	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
445	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
450	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
455	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
460	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
465	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
470	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
475	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
480	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
485	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	0.5
490	1	0.99	0.98	0.95	0.9	0.8	0.7	0.6	
495	1	0.99	0.98	0.95	0.9	0.8	0.7	0.620695	
500	1	0.99	0.98	0.95	0.9	0.8	0.7		

505	1	0.99	0.98	0.95	0.9	0.8	0.700431		
510	1	0.99	0.98	0.95	0.9	0.8	0.731128		
515	1	0.99	0.98	0.95	0.9	0.8	0.757994		
520	1	0.99	0.98	0.95	0.9	0.8			
525	1	0.99	0.98	0.95	0.9	0.803382			
530	1	0.99	0.98	0.95	0.9	0.822882			
535	1	0.99	0.98	0.95	0.9	0.840696			
540	1	0.99	0.98	0.95	0.9	0.857052			
545	1	0.99	0.98	0.95	0.9				
550	1	0.99	0.98	0.95	0.9				
555	1	0.99	0.98	0.95	0.9				
560	1	0.99	0.98	0.95	0.911088				
565	1	0.99	0.98	0.95	0.922317				
570	1	0.99	0.98	0.95	0.932715				
575	1	0.99	0.98	0.95	0.942553				
580	1	0.99	0.98	0.951777					
585	1	0.99	0.98	0.960357					
590	1	0.99	0.98	0.968431					
595	1	0.99	0.98	0.975989					
600	1	0.99	0.983081						
605	1	0.99	0.989736						
610	1								
615									

Rest of table 3:

X1 / P(MMHG)	0.4	0.3	0.25	0.2	0.1	0.05	0.02
400	0.4	0.3	0.25	0.2	0.1	0.05	0.02
405	0.4	0.3	0.25	0.2	0.1	0.05	0.02
410	0.4	0.3	0.25	0.2	0.1	0.05	0.02
415	0.4	0.3	0.25	0.2	0.1	0.05	0.02
420	0.4	0.3	0.25	0.2	0.1	0.05	0.02
425	0.4	0.3	0.25	0.2	0.1	0.05	0.02
430	0.4	0.3	0.25	0.2	0.1	0.05	0.02
435	0.4	0.3	0.25	0.2	0.1	0.05	0.02
440	0.4	0.3	0.25	0.2	0.1	0.05	0.02
445	0.4	0.3	0.25	0.2	0.1	0.05	0.02
450	0.4	0.3	0.25	0.2	0.1	0.05	0.02
455	0.4	0.3	0.25	0.2	0.1	0.05	0.02
460	0.4	0.3	0.25	0.2	0.1	0.05	0.02
465	0.4	0.3	0.25	0.2	0.1	0.05	0.02
470	0.4	0.3	0.25	0.2	0.1	0.05	0.02
475	0.4	0.3	0.25	0.2	0.1	0.05	0.02
480	0.4	0.3	0.25	0.2	0.1	0.05	0.02
485		0.3	0.25	0.2	0.1	0.05	0.02
490			0.229883	0.2	0.1	0.05	0.02
495					0.1	0.05	0.02
500					0.1	0.05	0.02
505					0.089274	0.05	0.02

510						0.05	0.02
515							0.02
520							
525							

Table 4-P-Y1 calculated data (A12=125.1797 & A21=-262.0684)

P (mmHg)	Y1	P (mmHg)	Y1
520	0	535	0.840696
515	0.02	540	0.857052
510	0.05	555	0.9
505	0.089274	560	0.911088
490	0.22983	565	0.922317
485	0.3	570	0.932715
485	0.5	575	0.942553
495	0.620695	580	0.951777
505	0.700431	585	0.960357
510	0.731128	590	0.968431
515	0.757994	595	0.975989
525	0.803382	600	0.983081
530	0.822882	605	0.989736

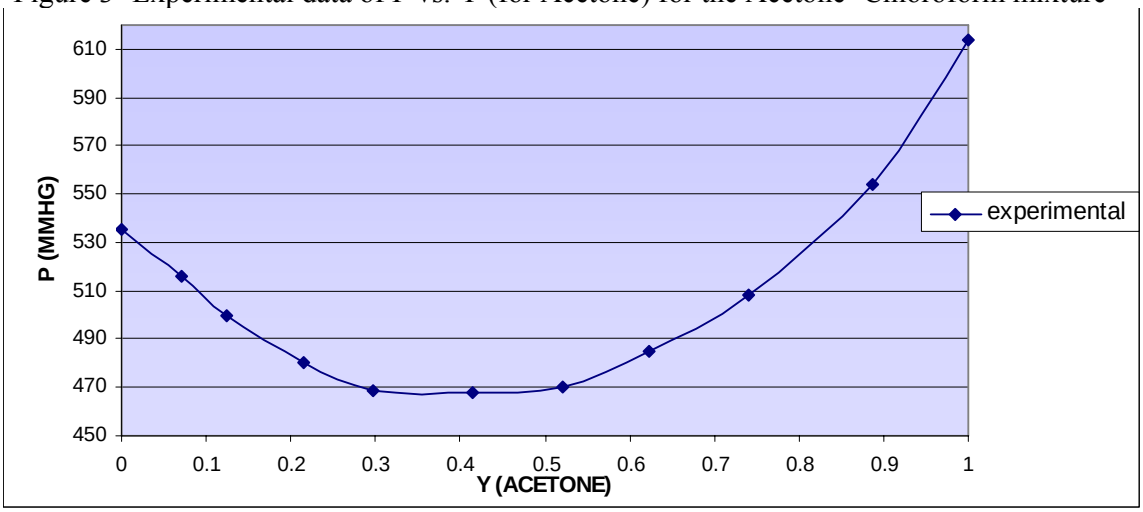
Table 5-P-Y1 Dechema experimental data

P (mmHg)	535	516	500	480	469	468	470	485	508	554	614
Y1	0	0.07	0.125	0.215	0.298	0.415	0.521	0.622	0.741	0.887	1

Table 6- P-Y1 Azeotropic handbook experimental data

P(bar)	P (MMHG)	Y1
60	450.1481	0.353
60.55	454.2744	0.376
60.67	455.1747	0.358
60.67	455.1747	0.374
60.7	455.3998	0.364
60.85	456.5252	0.361
62.33	467.6288	0.3575

Figure 3- Experimental data of P vs. Y (for Acetone) for the Acetone- Chloroform mixture



Range of Boiling Point Pressure

The range of Boiling point pressure of the feed depends on the Acetone mole percent in it. The range of boiling point while A12=125.1797 & A21=-262.0684 is as table 9:

Table 7- Range of Boiling Point Pressure

Acetone mole percent in the feed	Range of Boiling point pressure (mmHg)	
0.98	600-605	*Decrease*
0.95	580-595	
0.9	560-575	
0.8	560-575	
0.7	505-515	
0.6	495	
0. 5	485	
0.4	*480*	
0.3	485	*Increase*
0.25	490	
0.1	505	
0.05	510	
0.02	515	

Figure 4- Comparing the calculated data with the experimental ones (A12= -295.3605 & A21= 109.7564)

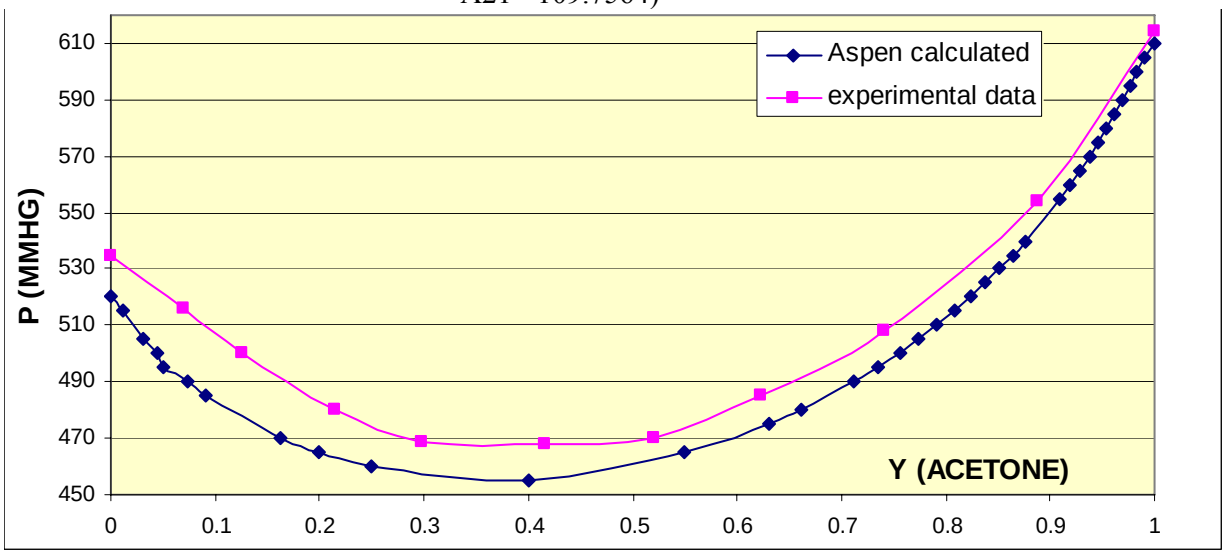
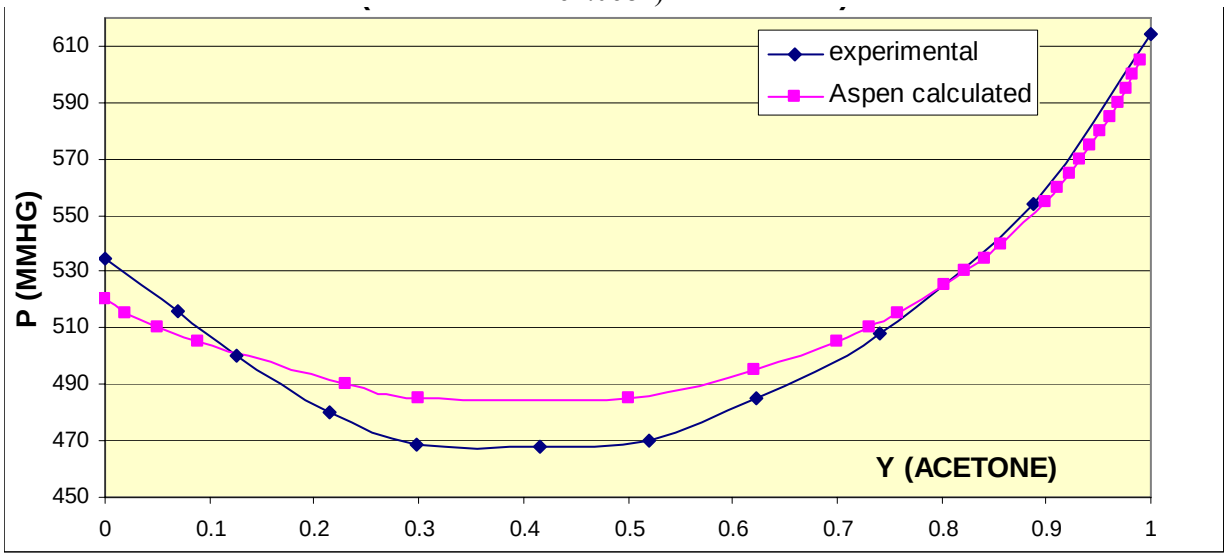


Figure 5- Comparing the calculated data with the experimental ones (A12= -125.1797 & A21= -262.0684)



Figures 4 and 5 show that the P-Y1 curve has a minimum at Y1=0.4. Which means we have an azeotropic mixture so at X1=Y1=0.4 the dew point and bubble point curves are tangent to the same horizontal line.

4. Results and Discussion

- A binary mixture of Chloroform and Acetone exhibits a minimum pressure azeotropic behavior which can be observed by their bubble point curve. P-Y1 curve of the binary mixture of Chloroform and Acetone has a minimum at Y1=0.4

- Comparing figure 4 and 5, the A12=125.1797 and A21=-262.0684 give better results (Closer to experimental data)
- Binary coefficients play a great role in the accuracy of the results
- The calculated P-Y1 is not exactly the same as the experimental ones because of the incompleteness of selected equation of state or maybe the binary coefficients are not exact enough. Totally it can be said that The Aspen modeling results are in good agreement with the experimental data.
- By using the Aspen software we can predict the mixtures' behavior

References

1- Jurgen Gmehling, U. Onken. Vapor- liquid equilibrium data collection: Aromatic hydrocarbons. Dechema

2- J. M. Smith, H.C. Van Ness, M. M. Abbott, Introduction to chemical engineering thermodynamics. McGraw-Hill

3 - Wikipedia encyclopedia

4- Moore, Walter J. Physical Chemistry, 3rd ed., Prentice-Hall 1962, pp140-142

5- Hilmen, Eva-Katrine (November 2000). Separation of Azeotropic Mixtures: Tools for Anaylsis and Studies on Batch Distillation Operation. Norwegian University of Science and Technology, dept. of Chemical Engineering. Retrieved on 24 March 2007.

6- Dominic Foo Chwan Yee, Distillation for azeotropic mixture, Chemical Engineering Tools and Information, 2004

7- Merck Index, 11th Edition, 58.

8- Srebnik, M.; Laloë, E. "Chloroform" Encyclopedia of Reagents for Organic Synthesis" 2001 John Wiley. DOI: 10.1002/047084289X.rc105

9- Ganesh Kamath and Jeffrey J. Potoff., Molecular Modeling of Phase Behavior and Structural Properties for Acetone-Chloroform-Methanol Binary Mixtures, Engineering Sciences and Fundamentals, 2005

10- Azeotopic Distillaion, Invision Power Board, 2004