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Liquid – vapour equilibrium calculations for MTBE/MEOH binary system by using Patel & Teja equation of state

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Abstract

This work presents vapour-liquid equilibrium calculations for a binary system, which is based on a computer program. For this purpose Patel & Teja equation of state has been used for the measurement of equilibrium data, which has high efficiency for polar systems. By using this program, various equilibrium datum such as bubble and dew point temperature/ pressure, flash calculations, and equilibrium coefficient (k value) could been calculated. The flowchart of this program and many applied example for MTBE/MEOH system are presented in this article and conclusions are reflected as graphs and tables.

Key words: modelling; equilibrium, Patel & Teja equation of state, k_{ij}, flash, bubble and dew point

Introduction

Thermodynamics and equilibrium datum are needed for design operating units such as distillation column, extraction and so on. The fallowing two methods are exist:

1) Experimental and laboratory methods

2) Calculating methods (Activity coefficient and equation of state)

Datum that will obtained with experimental methods are the most reliable, but calculating methods have preference to laboratory methods because of expensiveness and long time. In activity coefficient Method two separate thermodynamic models would be used for liquid phase activity coefficient and vapour phase fugacity coefficient and because of that to result in thermodynamic incompatibility. This model is used for polar systems, but because of above motioned reason is not recommended. Equation of state method has preference to activity coefficient Method, because only one equation is used for components fugacity coefficient in liquid and vapour phases but the best equation of state with high efficiency must be selected for system. Here PT equation of state has been used that is one of the best equations and has application for polar systems.

P&T equation of state

This equation is a 3rd order equation of state that has presented in 1982, and it has 3 parameters that are related to critical properties by fallowing equations:

$$P = \frac{RT}{v-b} - \frac{\alpha}{v(v+b)+c(v-b)} \quad (1)$$

$$a = \Omega_a.\left(R^2T_C^2 / P_C\right).\alpha \quad (2)$$

$$b = \Omega_b.\left(RT_C / P_C\right) \quad (3)$$

$$c = \Omega_C.\left(RT_C / P_C\right) \quad (4)$$

$$\Omega_C = 1 - 3\xi_C \quad (5)$$

$$\Omega_a = 3\xi_C^2 + 3\left(1-2\xi_C\right).\Omega_b + \Omega_b^2 + 1 - 3\xi_C \quad (6)$$

$$\Omega_b^3 + \left(2-3\xi_C\right).\Omega_b^2 + 3\xi_C^2.\Omega_b - \xi_C^3 = 0 \quad (7)$$

That Ω_b is the smallest positive root of above equation, and α is presented by soave and peng-Robinson equation:

$$\alpha = \left[1 + m(1 - T_R^{0.5})\right]^2 \quad (8)$$

m and ξ_C parameters are obtained by numerical methods and quantities of these parameters for MTBE/MEOH system are shown in table 1.

For multi-component systems, mixing rules should be used. For P&T equation of state, these equations are as fallow:

$$a_m = \sum_i \sum_j x_i.x_j.a_{ij} \quad (11)$$

$$b_m = \sum_i x_i.b_i \quad (12)$$

$$C_m = \sum_i x_i.c_i \quad (13)$$

$$a_{ij} = k_{ij}\left(a_{ii}.a_{jj}\right)^{1/2} \quad (14)$$

k_{ij} parameters namely binary interaction coefficient are experimental parameter and are calculated by using equilibrium data in binary systems. k_{ij} quantity for MTBE/MEOH system is 1.010.

Computer Program Flowchart

For bubble point temperature /pressure calculations, the fallowing equations are confirmed:

$$y_i = k_i.x_i \qquad i = 1, N \quad (15)$$

$$\sum y_i = 1 \qquad i = 1, N \quad (16)$$

N is number of components and y_i, x_i are mole fraction in vapour and liquid phases.

Similarly, for dew point calculations, the following equations are confirmed:

$$x_i = y_i / k_i \qquad i = 1, N \quad (17)$$

$$\sum x_i = 1 \qquad i = 1, N \quad (18)$$

For calculating of k value, Flash calculations as following equation are used.

$$F.z_i = V.y_i + L.x_i \quad (19)$$

F is feed mole rate; z_i feed mole fraction; V, L in order are component mole rate in equilibrium vapour and liquid phases.

This equation will obtain with overall mass balance and fallowing equations should be confirmed:

$$y_i = k_i.x_i \quad (20)$$

$$\sum y_i = 1 \quad (21)$$

$$\sum x_i = 1 \quad (22)$$

$$x_i = \frac{z_i}{L/F + V.k_i/F} \quad (23)$$

The flowchart of bubble point and flash calculations are shown in Fig 1 & 2. In order to know more about that, refer to reference (4).

Equations of Fugacity calculation are in Appendix A. In flash calculations, note that to guess first ki, ideal quantities are used (Wilson equation):

$$k_i = \frac{P_{vi}}{P} = \frac{P_{Ci}}{P} Exp\left[\frac{5.4(1+\omega_i)}{1-T_{Ci}/T}\right] \qquad W.eq. \quad (24)$$

Discussion and results:

For show prepared computer program efficiency, MTBE/MEOH binary system is selected and results are compared with experimental datum, that conclusions are in related tables and figures. Results for bubble point pressure/temperature calculations are shown in tables 2&3. As it is seeing, absolute deviation average in pressure/ temperature and mole fraction are less than 5 percent.

Conclusions for dew point temperature/pressure calculations are shown in tables 3&4.

Deviation in pressure and temperature for bubble and dew points are shown in Fig. 3,4,5,6 as graphs. Just as tables and graphs are saw, PT equation of state will be able to cover experimental points as well. Thus it is good for design calculations in MTBE system.

Component	T_c (^oR)	P_c (psia)	ω	M.W.	ζ_c	m
Methanol	922.752	1173.622	0.556	32.04	0.272	0.972708
MTBE	893.52	488.91	0.269	88.15	0.310	0.783340

Table 1: Thermodynamic and physical properties

$P_{exp.}$ (Psia)	$X_{i,exp.}$ MTBE	$Y_{i,exp.}$ MTBE	$P_{cal.}$	$Y_{i,cal.}$	Abs. Dev. P	Abs. Dev.Y
10.46	0.1024	0.2941	11.97	0.3758	0.1444	0.0817
12.05	0.2240	0.3857	12.73	0.4319	0.05643	0.0462
12.02	0.2246	0.4190	12.78	0.4326	0.06323	0.0136
12.95	0.2224	0.5151	12.80	0.4325	0.01158	0.0826
13.55	0.4854	0.6121	13.41	0.5293	0.01033	0.0828
13.70	0.6238	0.6711	13.48	0.6108	0.01606	0.0603
13.82	0.7475	0.7460	13.31	0.7086	0.03690	0.0373
13.83	0.7523	0.7384	13.30	0.7130	0.3832	0.0254
13.31	0.8761	0.8177	12.87	0.8381	0.3306	0.0204
13.50	0.8769	0.8018	12.88	0.8390	0.0452	0.0372
Total%					%4.56	%4.87

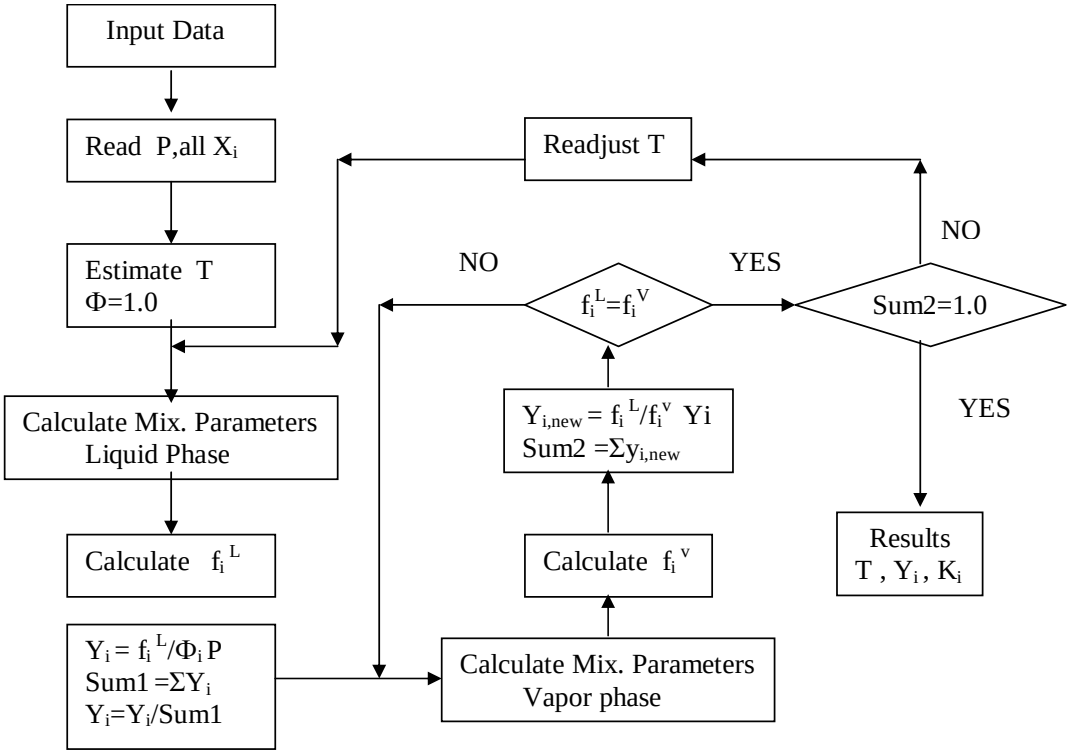


Fig.1 – Flowchart for bubble point calculations

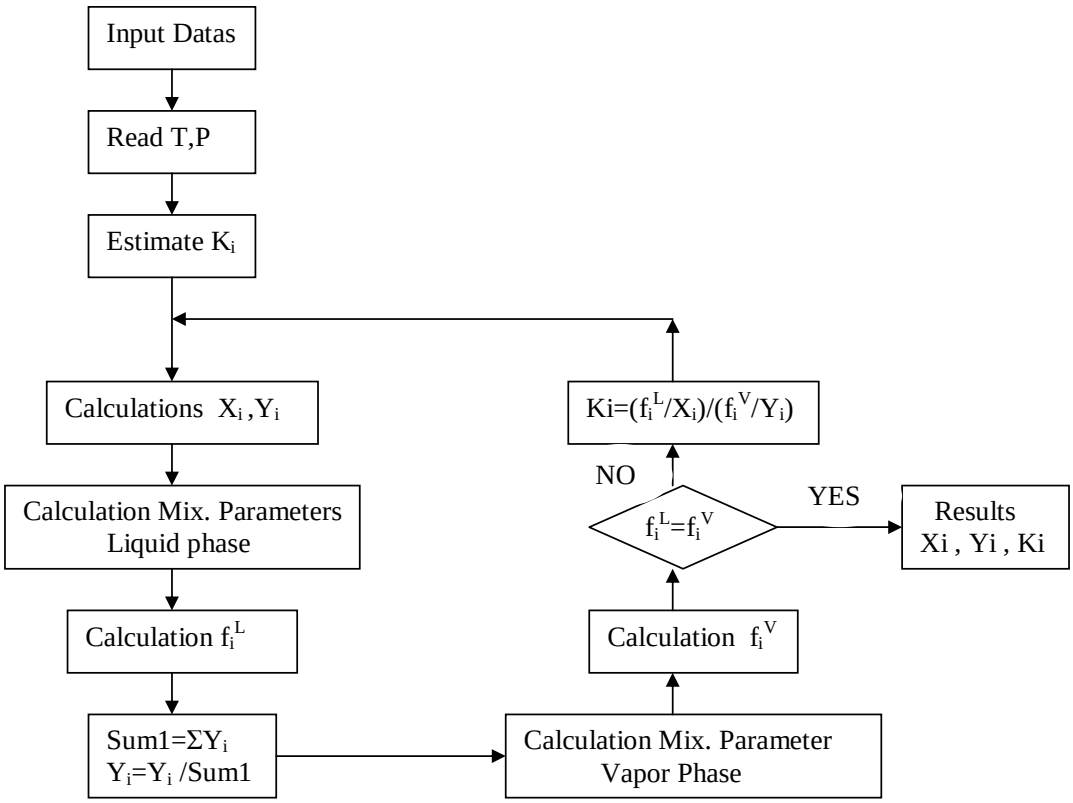


Fig.2 – Flowchart for flash calculations

Table2: Bubble point pressure calculations for MTBE/MEOH system (T= 581.35 ^{o}R)

$P_{exp.}$ (Psia)	$X_{i,exp.}$ MTBE	$Y_{i,exp.}$ MTBE	T_{cal} (^{o}R)	$Y_{i,cal.}$	Abs. Dev. P	Abs. Dev.Y
10.46	0.1024	0.2941	574.39	0.3973	0.01197	0.1032
12.05	0.2240	0.3857	578.37	0.4396	0.005126	0.0539
12.02	0.2246	0.4190	578.05	0.4416	0.005674	0.0226
12.95	0.2224	0.5151	581.97	0.4370	0.001066	0.0781
13.55	0.4854	0.6121	581.92	0.5289	0.0009805	0.0832
13.70	0.6238	0.6711	582.26	0.6106	0.001565	0.0605
13.82	0.7475	0.7460	583.36	0.7073	0.003457	0.0387
13.83	0.7523	0.7384	588.43	0.7115	0.003578	0.0269
13.31	0.8761	0.8177	583.12	0.8378	0.003045	0.0201
13.50	0.8769	0.8018	583.86	0.8385	0.004318	0.0267
Total%					% 0.4078	%5.239

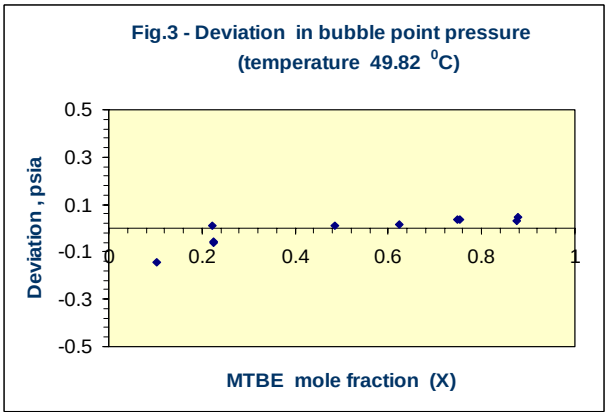
Table 3: Bubble point temperature calculations for MTBE/MEOH system ($T_{exp.}$ = 581.35 ^{o}R)

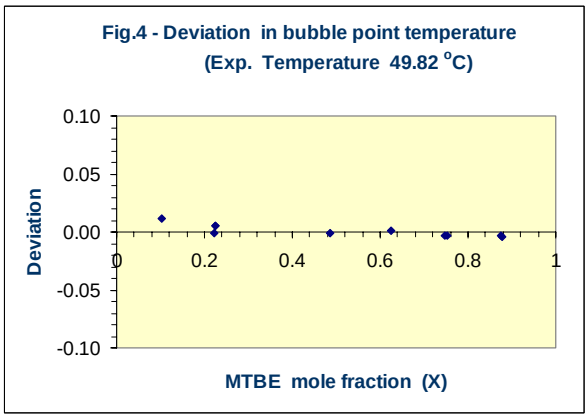
$P_{exp.}$ psia	$X_{i,exp.}$ MTBE	$Y_{i,exp.}$ MTBE	$P_{cal.}$	$X_{i,cal.}$	Abs. Dev. P	Abs. Dev. X
6.85	0.0955	0.2731	6.81	0.0267	0.005839	0.0688
6.81	0.1010	0.2995	7.01	0.0329	0.02937	0.0681
8.17	0.2071	0.4162	8.20	0.0845	0.003672	0.1226
8.10	0.2247	0.4425	8.51	0.1167	0.05062	0.102
8.70	0.3460	0.5293	9.18	0.4407	0.05517	0.0947
8.67	0.3507	0.5502	9.24	0.4896	0.06574	0.1389
9.26	0.4881	0.6198	9.38	0.6137	0.01296	0.1256
9.39	0.6177	0.6855	9.31	0.7071	0.008520	0.0894
9.51	0.7451	0.7434	9.24	0.7767	0.02839	0.0316
9.28	0.8704	0.8512	9.03	0.8832	0.02694	0.0128
Total%					% 2.87	%8.605

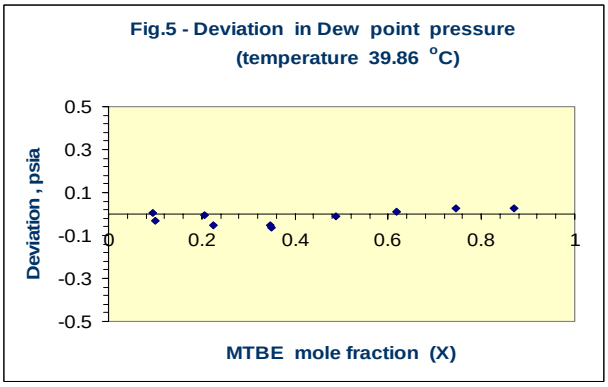
Table4: Dew point pressure calculations for MTBE/MEOH system($T_{exp.}$ = 563.42 ^{o}R)

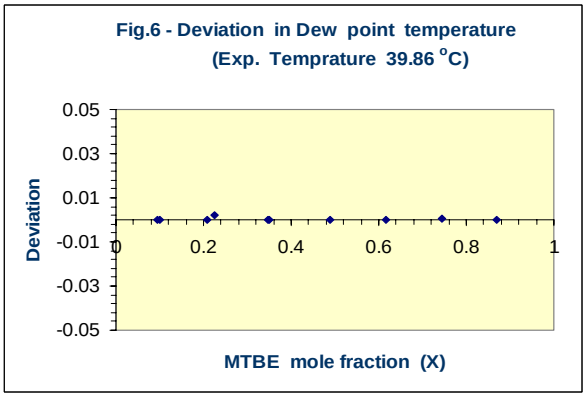
$P_{exp.}$ psia	$X_{i,exp.}$ MTBE	$Y_{i,exp.}$ MTBE	$T_{cal.}$	$X_{i,cal.}$	Abs. Dev.T	Abs. Dev.X
6.85	0.0955	0.2731	563.15	0.0742	0.000125	0.0313
6.81	0.1010	0.2995	561.94	0.0895	0.000109	0.0115
8.17	0.2071	0.4162	563.39	0.0947	0.000217	0.1124
8.10	0.2247	0.4425	561.52	0.1174	0.00190	0.1073
8.70	0.3460	0.5293	560.96	0.2478	0.000145	0.0982
8.67	0.3507	0.5502	560.51	0.4278	0.000226	0.0771
9.26	0.4881	0.6198	562.99	0.4780	0.000224	0.0101
9.39	0.6177	0.6855	563.91	0.7048	0.000161	0.0871
9.51	0.7451	0.7434	564.85	0.7730	0.000584	0.0279
9.28	0.8704	0.8512	564.76	0.8834	0.0000240	0.013
Total%					% 0.0148	%5.659

Table 5: Dew point temperature calculations for MTBE/MEOH system ($T_{exp.}$ = 563.42 ^{o}R)









Appendix A

The equations for fugacity calculation by P&T equation of state:

a) Component fugacity in pure case:

$$In(\frac{f}{p}) = Z - 1 - In(Z - B) + \frac{a}{2RTN} In(\frac{Z + M}{Z + Q})$$

$$B = \frac{bP}{RT}$$

$$M = \frac{b + c}{2 - N} \cdot \frac{P}{RT}$$

$$N = \left[bc + \frac{(b + c)^2}{2} \right]^{-0.5}$$

$$Q = \frac{b + c}{2 + N} \frac{P}{RT}$$

b) Component fugacity in mixture:

$$RTIn(\frac{f_i}{x_i P}) = -RTIn(Z - B) + RT(\frac{b_i}{v - b}) - \frac{x_i \ a_{ij}}{d} In(\frac{Q + d}{Q - d})$$

$$+ \frac{a(b_i + c_i)}{2(Q^2 - d^2)} + \frac{a}{8d^3} \{c_i(3b + c) + b_i(3c + b)\} \left\{ In(\frac{Q + d}{Q - d}) + \frac{2Qd}{Q^2 - d^2} \right\}$$

$$Q = V + \frac{b+c}{2}$$

$$B = \frac{bP_c}{RT_c}$$

$$d = \left[bc + \frac{(b+c)^2}{4} \right]^{0.5}$$

Abbreviations

a, b, c , m ,α ,ζ , Ω : PT equation of state parameters
f : fugacity
Φ: fugacity coefficient
K_{ij}: interaction coefficient
N: number of components
P: pressure
T: temperature
v : volume
R: universal gas constant
F: feed mole rate
L: liquid phase mole rate
V: gas phase mole rate
X: component mole fraction in liquid phase.
Y: component mole fraction in vapour phase.
Z: component mole fraction in feed.

Subscript

C: Critical properties
i,j: Component No.
m: mixture
Superscript:
L: Liquid phase properties
V: Vapour phase properties

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