Modeling of Vapor Liquid Equilibrium Data for Thyme Essential Oil Based on UNIQUAC Thermodynamic Model

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ABSTRACT

Vapor Liquid Equilibrium (VLE) data for natural ingredients and essential oils has not studied at all yet. It is because of the complexity of these mixtures. In this study, the equilibrium concentration of the mixture components was studied by using UNIQUAC model at different pressures. This model is capable of determining the temperature between 70 ℃ to 170 ℃ and the pressure limits 30 Kpa to 202 Kpa. The Modeling results showed Thymol in the liquid phase was increased from 50% molar to 90% molar in constant pressure by increasing the temperature from bubble point to dew point temperature. Thymol concentration in the liquid phase was increased from 42% molar to 78% molar by increasing the water concentration of the mixture at a constant pressure of 100 Kpa and constant temperature 177 ℃. Another obtaining result showed that Thymol concentration in the triple mixture, which includes 30% molar water, 35% molar Thymol, and 35% molar Cymene in liquid phase, was increased from 60% molar to 82% molar at constant temperature of 177 ℃ by decreasing the pressure from 100 Kpa to 20 Kpa.

KEYWORDS: Essential oil, VLE, UNIQUAC, Modeling

1. Introduction

Thymus vulgaris plants of the family lamiaceae are fragrant [1]. Distribution of 215 species worldwide and 14 species of Thymus vulgaris has been reported in Iran [2]. This plant food is as traditional as digestive, antispasmodic, and antitussive due to the main compound Thymol, in the food industry, pharmaceutical, health and beauty uses [3]. The aqueous extract, aqueous Ethanol and Propylene Glycol are used in the preparation of Thymus Vulgaris shampoo, creams and ointments [4]. This plant's antifungal effects, antibacterial and ant parasite, and its therapeutic efficacy for the treatment of asthma, recurrent dry cough, and bronchitis have been proved. This medical plant syrups and pills have been incensed, and extracts have been prepared and approved by the drug unit of supervision, ministry of health and medical education [5]. The treatment plant, flowering shoot and its leaves are dried. World wages species Thymus Vulgaris (Thymus Daensis Celak) are distributed in different regions of Qazvin province. This plant is propagated by seeds and can be divided. As Table 1 showed, Thymol is the main compound of Thymus Vulgaris plant and the molar amount of Thymol dittany has been reported about 40% to more than 70% of the world wages. Based on the results of extraction thymus Vulgaris world wages sample collected from Hamedan which includes 26 compounds 95.1% of the Thymol with 44.7%, Para Cymene with 18.6% and Alpha Terpinene with 16.5% in most combinations [6]. Garden thymus vulgaris (Thymus Vulgaris) is grown in large areas of farmland in Europe, North Africa and the United States every year. The essential oils yield is 2 to 3 percent and Thymol in the essential oil has been reported about 40 to 65 percent [7].

1.1 Gas chromatography

Chemical analysis was performed on a Hewlett–Packard 5890 series II ; gas chromatograph fitted with a HP-5 capillary column (25m×0.20mm, film thickness 0.33 μm). The carrier gas was hydrogen at a flow of 1.0 ml min-1 and a split ratio 1:100. The column temperature was programmed from 60–250 ℃ at 2.0 ℃ min-1; the injector temperature was 250 ℃ and the detector (FID) temperature was 280 ℃ [8].

1.2 Gas chromatography/mass spectroscopy

The analysis was performed on a Hewlett–Packard 5890 series II gas chromatograph coupled to a HP 5970 mass selective detector using a fused silica capillary column HP-5 (25 m×0.20 mm, film thickness 0.33 μm). The column temperature was programmed from 60–250 ℃ at 2.0 ℃ min-1 using helium as the carrier gas at a flow rate of 1.0 ml min-1. The ion source temperature was 300 ℃ and the electron energy 70 eV. Identification of components was based on comparison of their mass spectra with those found in the literature

on retention indices, the mass spectrometry data bank (NIST), and a computer search of the Wiley library [8].
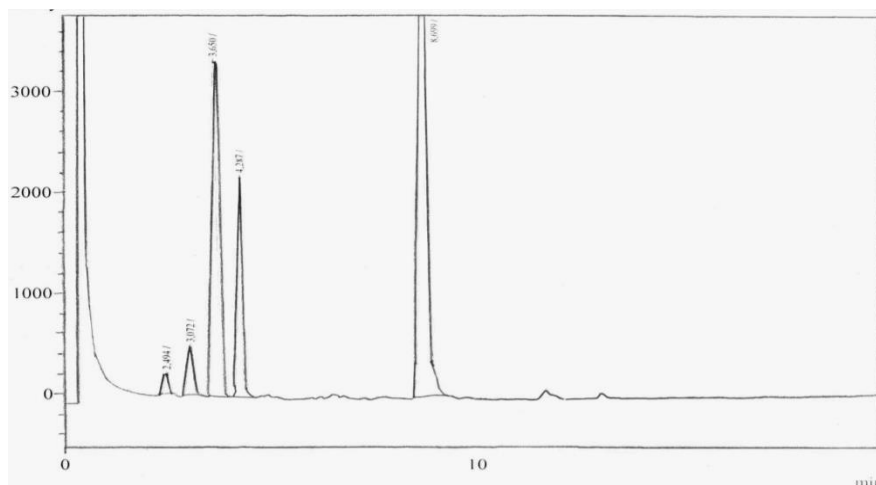

Figure1. Chromatogram of the thyme essential oil

Table1. The type and composition of thyme essential oil

NO#	NAME	RI	Percent %
1	Tricyclene	925	0.53
2	β-Pinene	928	0.18
3	α-Tujene	931	0.33
4	Camphene	945	0.32
5	Myrcene	992	0.887
6	α-phlladrene	1005	0.13
7	α-Terpinene	1016	0.75
8	P-Cymene	1027	4.6
9	Limonene	1032	0.33
10	Carvacrol	1035	1.4
11	1,8-Cineole	1043	1.64
12	γ-Terpinene	1062	4.48
13	Cis-Sabinene Hydrate	1074	0.8
14	Terpinolene	1088	0.12
15	Trans-Sabinene Hydrate	1097	0.27
16	Borneol	1164	1.61
17	Terpinene-4-Ol	1188	0.57
18	Carvacrol/Methyl Ether	1246	4.27
19	Thymol	1297	73.61
20	β-Caryophylene	1416	0.99
21	Germacrene B	1487	0.64
22	α-Murolene	1499	0.94
23	β-Bisabolene	1509	0.17
24	δ-Cadinene	1525	0.16

2. Modeling the Vapor and liquid equilibrium

A number of important industrial processes such as distillation, absorption and extraction, makes two phases in contact with each other. Mass transfer between two phases occurs when the phases are not in equilibration. The amount and speed of transfer depend on the distance from the device and equilibrium. Quantitative analysis of mass transfer will require data and information about the equilibrium conditions (pressure, temperature, and mole fraction of components). In the most industrial processes, coexistence phases are of kinds of liquid and vapor; although, the liquid- liquid, vapor- solid and liquid-solid exists as well. This section is going to analyze and describe the qualitative and general behavior of the liquid and vapor phase in the essential oil distillation process, and calculate the temperature, pressure, and mole fraction of components for liquid and vapor equilibrium. Equilibrium is a static condition, which causes no changes in the main properties of a device. This is because of the balance between all factors that may cause changes. In engineering practice,

the equilibrium assumption is confirmed when the results would be satisfactory. For example, in the distillation column re-boiler, it is generally assumed that the equilibrium is established between vapor and liquid phases. This is an approximation for certain evaporation; although, this approximation in engineering calculations does not make an error. In a system with a constant amount of chemicals that contain vapor and liquid phases in close contact, there is no desire to change the system. Temperature, pressure, and phase components reach the final value and amount, and then remain constant. Therefore, the system is in equilibrium but at a molecular level, it is not a constant condition. Molecules forming one phase at a given moment are not the same as molecules in that phase in another moment. High speed molecules which are located near the boundary between the phases overcome the surface forces and go to another phase [9]. In vapor and liquid equilibrium condition the amount of molecules that leave the interface, and go to the vapor phase are equal with the number of another molecule component which returns to the liquid phase. Therefore, the concentration of each component in the vapor and liquid phase does not change during the time. Although, theoretically, equilibrium requires a long time, if the vapor liquid is placed vicinity and no reaction occurs between them, the equilibrium will come quickly.
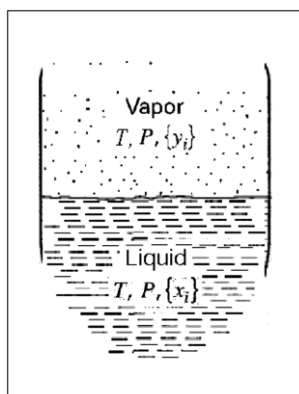

Figure2. Schematic representation of VLE

According to thermodynamic relations, the equilibrium condition is the equality of chemical potential of component i in liquid and vapor phase in a constant temperature and pressure [10].

Macroscopic state of liquid vapor equilibrium is in constant temperature and pressure that, the chemical potential of each component in liquid phase equals to the chemical potential of each component in vapor phase [11].

$$(T, P) = cte \quad \mu_i^V = \mu_i^L \tag{1}$$

On the other hand, with the help of the following thermodynamic relations, the chemical potential of each component in the liquid phase can associate to fugacity and activity coefficient of each component in the liquid phase. For complex mixtures such as essential oils, using fugacity model for both vapor and liquid phase for predicting equilibrium data is necessary. Therefore, suitable activity model is used for liquid phase [12].

$$d\mu_i^V = RTd \ln f_i^V \tag{2}$$

$$d\mu_i^L = RTd \ln f_i^L \tag{3}$$

Thus, we have the equilibrium condition:

$$f_i^V = f_i^L \tag{4}$$

If f_i^V, f_i^L values for each component are in the vapor and liquid phase, the fugacity which is a pressure unit is used for two non-ideal phases. Fugacity for vapor phase is as follow [13].

$$f_i^V = \varphi_i . y_i . P \tag{5}$$

The amount of fugacity in the liquid phase is calculated from the following equation:

$$f_i^L = \gamma_i . x_i . f_i \tag{6}$$

$$\varphi_i . y_i . P = \gamma_i . x_i . f_i \tag{7}$$

The required equilibrium information is usually expressed by the K value [14]:

$$K_i = y_i / x_i \tag{8}$$

Where y_i is the mole fraction i in vapor phase and x_i is the mole fraction i in liquid phase. K_i is the equilibrium constant of component i at T temperature and P pressure [15].

By using thermodynamics, fugacity and activity coefficients can be related to the K value [16]:

$$K_i = \gamma_i \, f_i^0 \, / \, P \qquad \qquad \Phi_i \tag{9}$$

γ_i is the activity coefficient of component i in the liquid phase and Φ_i is fugacity coefficient of component i in the vapor phase and P is the total pressure of the mixture. For compressible components, f_i^0 is the pure fugacity of component i at T system temperature and P pressure [17]. Activity coefficients may be based on thermodynamic theory models, which are based on a rather strong scientific theory or an experimental model for example UNIQUAC, NRTL, UNIFAC, and Wilson [18].

$$\frac{G^E}{RT} = \qquad g(x_1, x_2, \dots, x_n) \tag{10}$$

$$\frac{G^E}{x_1 x_2 RT} = a + bx_1 + \qquad cx_1^2 + \cdots \tag{11}$$

$$G^E = \qquad RT \sum_i n_i \ln \gamma_i \tag{12}$$

$$RT \ln \gamma_i = \qquad \left(\frac{\partial n_i G^E}{\partial n_i} \right)_{T,P,n} \tag{13}$$

Equation UNIQUAC, with $\frac{G^E}{RT}$ consists of two additives, the case course seeks to put. The union sector $g^{c,}$ is for calculating the molecular size and shape differences. Other sector g^R is for calculating the molecule effects [19].

$$G = g^c + g^R \tag{14}$$

Function g^c only includes pure material parameters, while the function g^R includes the interaction of two parameters, which is formed for each pair of molecules.

For a multi-components system [20]:

$$g^c = \sum_i x_i \; ln\frac{\emptyset_i}{x_i} + \qquad 5 \sum_i q_i x_i \; ln\frac{\theta_i}{\emptyset_i} \tag{15}$$

$$\tag{16}$$

$$g^R = - \sum_i q_i x_i \; ln\left(\sum_i \theta_j \tau_{ji} \right) \tag{17}$$

$$\emptyset_i = \qquad \frac{x_i r_i}{\sum_j x_i r_i} \tag{17}$$

$$\theta_i = \qquad \frac{x_i q_i}{\sum_j x_j q_j} \tag{18}$$

i, represents the material and j is an index. All calculations is for all materials and the value τ is equal to 1 for i=j [21].

In these equations, r_i (relative molecular size) and q_i (relative molecular level), are pure material parameter [22]. The temperature dependence of g at the above equation is determined by the following equations [23]:

$$\tau_{ij} = \exp - \qquad \left(\frac{u_{ji} - u_{ii}}{RT} \right) \tag{19}$$

Interaction parameters in the UNIQUAC equation are $(u_{ji} - u_{ii})$. To obtain equation $\ln\gamma$, is as follow [24]:

$$\ln \gamma_i = \ln \gamma_i^c + \qquad \ln \gamma_i^R \tag{20}$$

$$\ln \gamma_i^c = 1 - j_i + \ln j_i - 5q_i \left(1 - \frac{j_i}{L} + \qquad \ln\frac{s_{ji}}{\eta_j} \right) \tag{21}$$

$$\ln \gamma_i^R = q_i(1 - \ln L_i) - \sum_j \left(\theta \frac{s_{ji}}{\tau_{ij}} - \right. \tag{22}$$

$$\left. q_i \ln \frac{s_{ji}}{\eta_j} \right)$$

$$J_i = \tag{23}$$

$$\frac{r_i}{\sum_j r_j x_j}$$

$$L_i = \tag{24}$$

$$\frac{q_i}{\sum_j q_j x_j}$$

$$\theta = \tag{25}$$

$$\sum_i q_i x_i$$

$$s_{ji} = \tag{26}$$

$$\sum_m q_i \tau_{mj}$$

$$\eta_j = \tag{27}$$

$$\sum_i s_{ji} x_i$$

$$\tau_{mj} = \tag{28}$$

$$\exp \left(\frac{u_{ij} - u_{ij}}{RT} \right)$$

In these equations i, is the material expression. M and j are counters. All calculations are for all materials and for m = j we have $\tau_{mj} = 1$ [25].

All calculations have been performed using MATLAB software [26], [27], [28], [29].

Values of parameters for the Margules, van Laar, and Wilson, NRTL, and UNIQUAC equations are given for many binary pairs by Gmehling [30].

3. Results and Discussions

In this section, the data is shown in a graph for Thymol component to achieve a better picture of the results. Diagrams show Thymol concentration in the liquid phase besed on the temperature and the pressure. This chart shows the change of Thymol concentration in the liquid phase based on the temperature. Each curve represents the change of concentration in certain pressure.
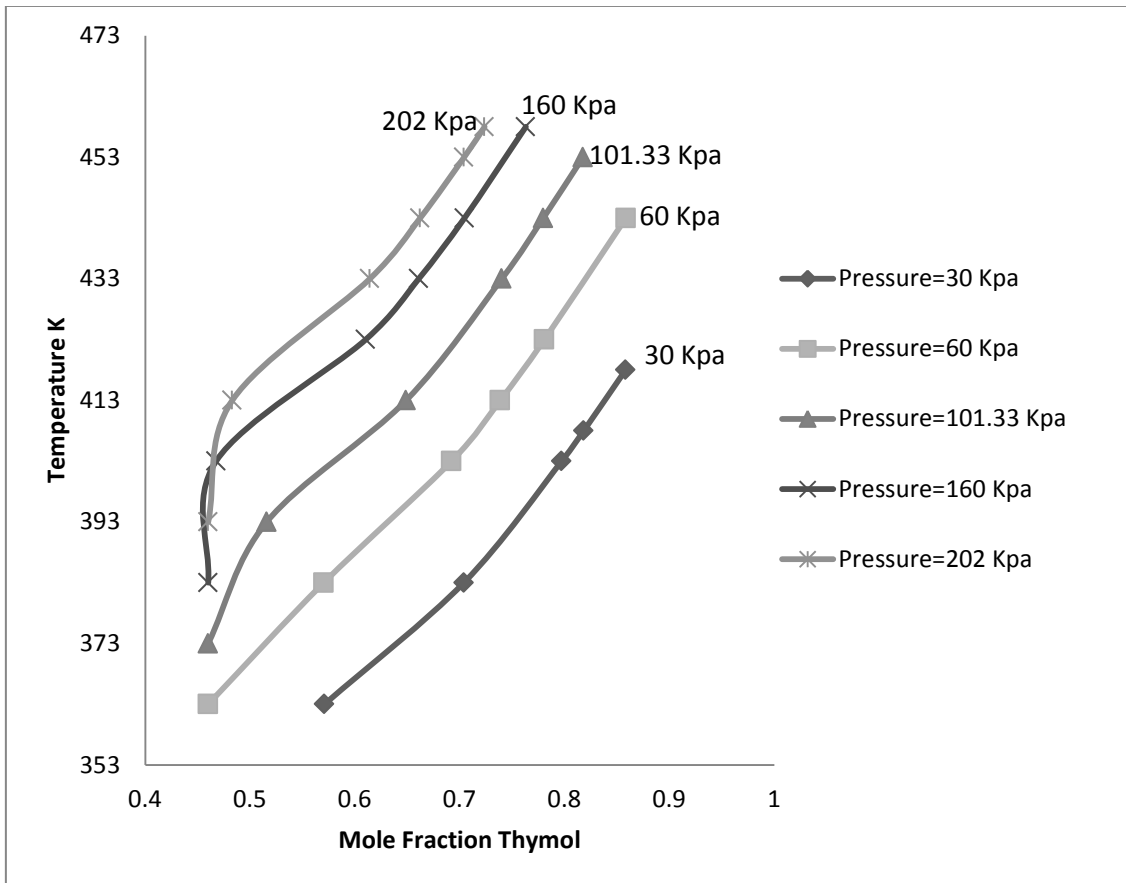
Figure3. Thymol concentration changes in the liquid phase depending on temperature at constant pressure

As you see in Figure (3), the concentration of Thymol in the liquid phase increases by increasing the temperature at constant pressure. At higher pressures, to achieve a certain amount of Thymol concentration, the higher temperature is required. Due to the sensitivity of plant compounds to temperature, low pressure is recommended. Changes of Thymol concentration in liquid phase depends on the pressure at constant temperature.
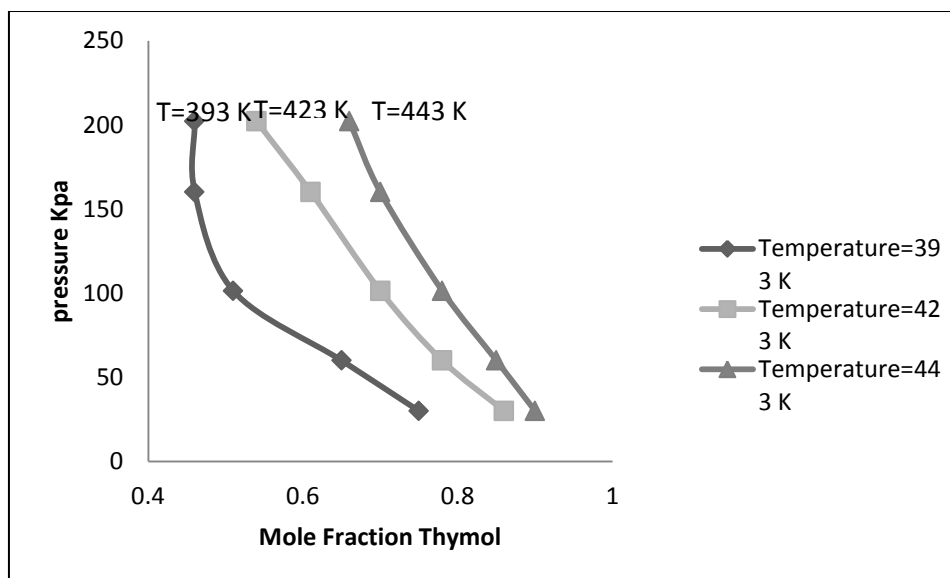

Figure4. Thymol concentration changes in the liquid phase, depending on the pressure at constant temperature

Figure (4) shows the changes of Thymol concentration in the liquid phase, depends on the pressure in certain temperatures. This figure shows that, by increasing the pressure at constant temperature, the amount of Thymol in the liquid phase decreases. In constant pressure at higher temperatures, the amount of Thymol in the liquid phase increases. As it is indicated in the chart, the highest concentration of Thymol is in the lowest pressure.
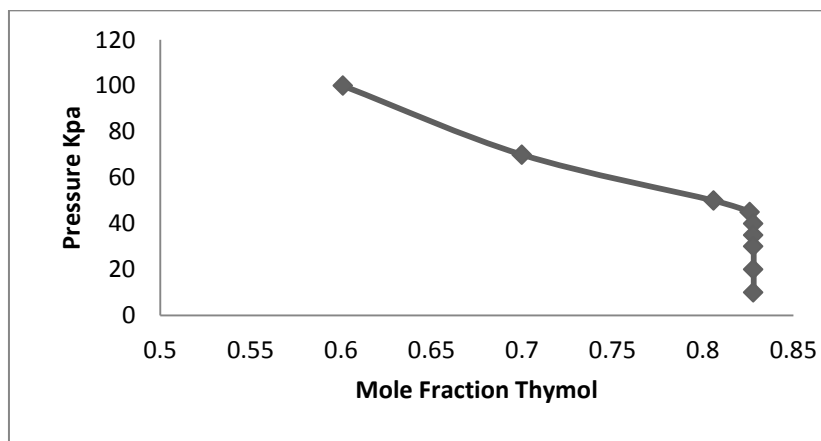

Figure5. Thymol concentration changes in terms of pressure, at constant temperature

In Figure (5), the triple mixture which includes 30% molar water, 35% molar Thymol, and 35% molar Cymene in liquid phase at constant temperature of 177 ℃, by decreasing the pressure from 100 Kpa to20 Kpa, Thymol concentration increases from 60% molar to 82% molar.
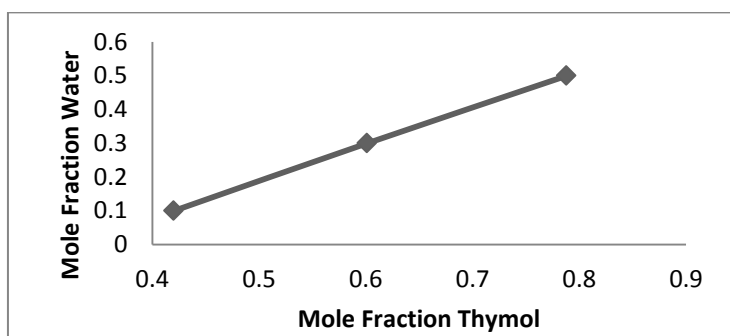

Figure6. Thymol mole fraction changes, depending on mole fraction of water changes

According to the Figure (6), Thymol concentration in the liquid phase was increased from 42% molar to 78% molar by increasing the water concentration of the mixture at a constant pressure of 100 Kpa and the constant temperature 177 ℃.

3.1 Discussions
According to the results of equilibrium data modeling and comparison on different pressures, the temperature and the water concentration, the following results were obtained.
1. By increasing the temperature of the bubble point to dew point temperature at constant pressure, Thymol concentration in the liquid phase increases.
2. By increasing the temperature at constant pressure, the amount of Thymol concentration in the liquid phase increases. At higher pressure, to achieve a certain amount of Thymol concentration, the higher temperature is required. Due to the sensitivity of the plant compounds to temperature, low pressure is recommended.
3. By increasing the pressure at constant temperature, the amount of Thymol in the liquid phase decreases. At constant pressure and higher temperatures, the amount of Thymol in the liquid phase increases.

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