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

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Abstract

Vapour Liquid Equilibrium (VLE) data for natural ingredients and essential oils has not studied at all yet. It is because of complexity of these mixtures. In this study, the equilibrium concentration of the mixture components was studied by using the UNIQUAC model at different pressure. This model is capable of determining temperature between 70°C to 170°C and the pressure limits 30 Kpa to 202 Kpa. The modeling's results showed thymol in the liquid phase were increased from 50% molar to 90% molar in constant pressure by increasing temperature from bubble point to dew point's temperature. Thymol concentration in the liquid phase was increased from 42% molar to 78% molar by increasing water concentration of the mixture at a constant pressure of 100 Kpa and constant temperature 177°C. 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°C by decreasing pressure from 100 Kpa to 20 Kpa.

Keywords: Thyme; Essential oil; VLE; UNIQUAC; Modeling; Thermodynamic phases

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 the digestive, antispasmodic, antitussive, and due to the main compound thymol, in the food industry, pharmaceutical, health and beauty uses [3]. The aqueous extract, aqueous Ethanol and Propylene Glycol in the preparation of *Thymus vulgaris* shampoo, creams and ointments are used [4]. This plant is antifungal effects, antibacterial and ant parasite and its therapeutic efficacy for treatment of asthma, recurrent dry cough and bronchitis has been proved. This medical plant, syrups, pill, incense and extracts were prepared and has 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 seed and can be divided. thymol is the main compound of *Thymus vulgaris* plant and the molar amount of thymol dittany have 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 the Hamedan which includes 26 compounds 95.1% of the thymol with 44.7%, Para Cymene with 18.6% and Alpha Trypen with 16.5% in most combinations [6]. Garden *Thymus vulgaris* every year in large areas of farmland in Europe, North Africa and the United states is grown. In Figure 1 and Table 1 the essential oils yield is 2 to 3 percent and thymol in the essential oil has been reported about 40 to 65 percent [7].

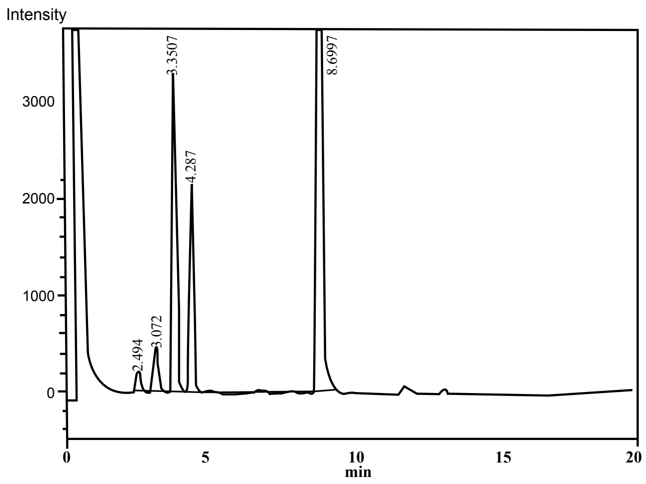

Figure 1: Chromatogram of the Thyme essential oil.

Gas chromatography

Chemical analysis was performed on a Hewlett–Packard 5890 series II gas chromatograph fitted with a HP-5 capillary column (25 m×0.20 mm, 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°C at 2.0°C min-1; the injector temperature was 250°C and the detector (FID) temperature was 280°C [8].

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°C

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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

Table 1: The type and composition of Thyme essential oil.

at 2.0°C min-1 using helium as the carrier gas at a flow rate of 1.0 ml min-1. The ion source temperature was 300°C 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].

Theory

Modeling the vapour and liquid equilibrium

A number of important industrial processes such as distillation, absorption, and extraction, make 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 vapour, although the liquid-liquid, vapour-solid and liquid-solid are also exist. This section is going to analyze and describe the qualitative and general behavior of the liquid and vapour phase in the essential oil distillation process, calculate the temperature, pressure and mole fraction of components for liquid and vapour equilibrium. Equilibrium is a static condition, which cause no change in the main properties of a device. This is because of the balance among 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 reboiler, it is generally assumed that the equilibrium is established between vapour 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 vapour and liquid phases that are in close contact, there is no desire to change the system. Temperature, pressure and phase component are reached to final value and amount, and then remain constant. So 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 as that phase in another moment. High speed molecules which are located near the boundary between the phases are overcome to the surface forces and go to another phase [9]. In vapour and liquid equilibrium condition the amount of molecules that leave the interface, and go to the vapour phase are equal with the number of another molecules component which returns to the liquid phase. Therefore, the concentration of each component in the vapour and liquid phase does not change during the time. Although theoretically, equilibrium required a long time, if the vapour liquid are placed vicinity and no reaction occurs between them, the equilibrium will come quickly (Figure 2).

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

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

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

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 mixture such as essential oils, using fugacity model for both vapour and liquid phase to 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: $f_i^V = f_i^L$ (4)

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

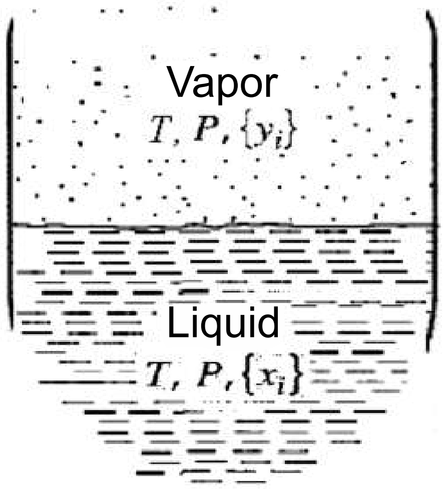

Figure 2: Schematic representation of VLE.

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

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]: $K_i = y_i / x_i$ (8)

Where y_i is the mole fraction (i) in vapour 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]:

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

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

$$\frac{G^E}{RT} = g(X_1, X_2 ....., X_n) \tag{10}$$

$$\frac{G^E}{X_1 X_2 RT} = a + bX_1 + cX_1^2 + ... \tag{11}$$

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

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

Equation UNIQUAC, with $\frac{G^E}{RT}$ and consists of two additive, the case course seeks to puts. The union sector g^c, for calculating the molecular size and shape differences. Other sector g^R, 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]:

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

$$g^R = -\sum_i q_i x_i \ln\left(\sum_i \theta_j \tau_{ji}\right) \tag{16}$$

$$\phi_i = \frac{x_i r_i}{\sum_j x_i r_i} \tag{17}$$

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

(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^R at the above equation is determined by the following equations [23]: $\tau_{ij} = \exp -\left(\frac{u_{ji} - u_{ii}}{RT}\right)$ (19)

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

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

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

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

$$J_i = \frac{r_i}{\sum_j r_j x_j} \tag{23}$$

$$L_i = \frac{q_i}{\sum_j q_j x_j} \tag{24}$$

$$\theta = \sum_i q_i x_i \tag{25}$$

$$s_{ji} = \sum_m q_i \tau_{mj} \tag{26}$$

$$\eta_j = \sum_i s_{ji} x_i \tag{27}$$

$$\tau_{mj} = \exp\left(\frac{u_{ij} - u_{ij}}{RT}\right) \tag{28}$$

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

All calculations have been performed using MATLAB software [26-28].

Values of parameters for the Margules, van Laar, and Wilson, NRTL, and UNIQUAC equations are given for many binary pairs by Gmehling [29].

Discussion

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 according to temperature and pressure. This chart shows the change of thymol concentration in the liquid phase that is depending on temperature, and each curve represents the change of concentration in certain 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 sensitivity of plant

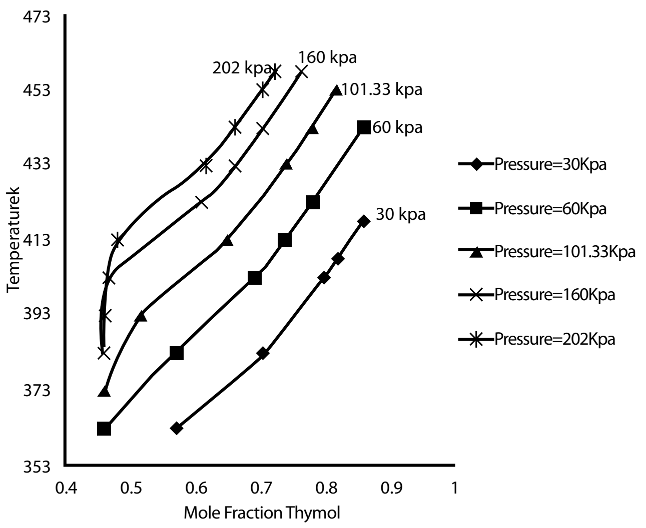

Figure 3: Thymol concentration changes in the liquid phase depending on temperature at constant pressure.

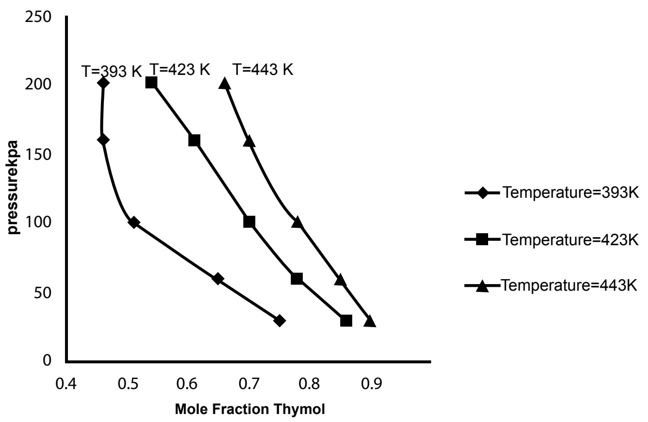

Figure 4: Thymol concentration changes in the liquid phase, depending on pressure at constant temperature.

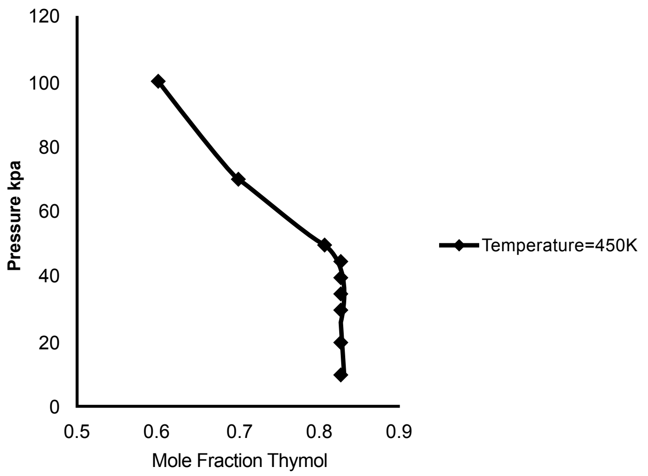

Figure 5: Thymol concentration changes in terms of pressure at constant temperature.

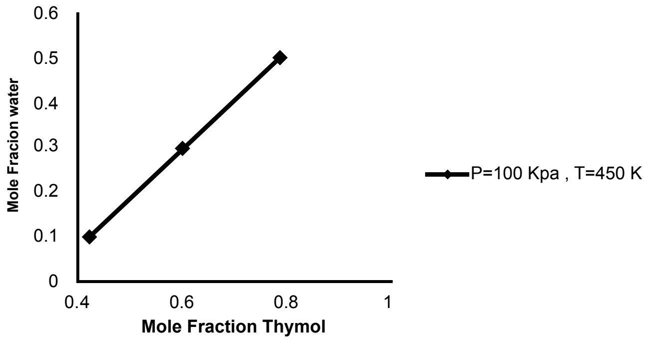

Figure 6: Thymol mole fraction changes depending on mole fraction of water changes.

compounds to temperature, low pressure is recommended. Change of thymol concentration in liquid phase depending on pressure at constant temperature.

Figure 4 shows the changes of thymol concentration in the liquid phase, depending on pressure in certain temperatures. This figure shows that by increasing 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.

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

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

Conclusions

According to the results of equilibrium data modeling and comparison on different pressure, temperature and water concentration, the following results were obtained.

1. By increasing temperature of the bubble point to dew point temperature at constant pressure, thymol concentration in the liquid phase is increasing.
2. By increasing 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 sensitivity of plant compounds to temperature, low pressure is recommended.
3. By increasing 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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