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

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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].

\[(T, P) = \text{cte} \mu_i^L = \mu_i^V\]  

(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].

\[d \mu_i^L = RT \ln f_i^L\]  

(2)

\[d \mu_i^V = RT \ln f_i^V\]  

(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].
\[ f_i^e = \phi_i^c \gamma_i \theta_i \]  
(5)

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

\[ f_i^e = \gamma_i \theta_i \phi_i^c x_i \]  
(6)

\[ \phi_i^c \gamma_i \theta_i = \gamma_i \theta_i \]  
(7)

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

\[ K_i = \frac{\gamma_i}{x_i} \]  
(8)

Where \( \gamma_i \) 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]:

\[ \gamma_i = \sum \frac{x_i}{\theta_j} \]  
(9)

\[ \gamma_i = \sum x_i \]  
(10)

Equation UNIQUAC, with \( \frac{G^e}{RT} \) and consists of two additive, the case course seeks to puts. The union sector gc, for calculating the molecular fraction (i) in liquid phase. Ki is the equilibrium constant of component (i) represents the material and (j) is an index. All calculations is for all materials and the value \( \tau \) is equal to 1 for \( i=j \) [21].

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
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 at constant temperature. 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 to 20 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.

References

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