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Dynamic and static solubility of thymoquinone in the supercritical carbone dioxide

Introduction

Thymoquinone (TQ) is a biologically active component, used for treatment of many different illnesses, such as a diarrhea, bronchial asthma and as a cancer therapy. Important natural of TQ is essential oil of black cumin seeds, also known as *Nigella Sativa* Linn. [*Paarakh, 2010*]. Essential oil has its volatile fraction, which can be extracted from seeds by organic solvents. There is no available date of solubility TQ in the usual hydrocarbons and alcohols solvents. However, these solvents are often used in the conventional methods of extraction. [*Brunner, 1994*]. Such solvents are flammable and many of them are toxic. Supercritical carbon dioxide extraction is an alternative and a very promising method for separation of essential volatile oil from black cumin. The process has several advantages over conventional methods. It uses a non-harmful supercritical carbone dioxide, the extract does not need post processing, and composition of extract is rich with volatiles

Solubility measurements are necessary for process design of extraction. There are several techniques to measure solubility [*Gupta and Shim, 2007*]. All of the methods can be divided into the main classes: dynamic and static. In dynamic methods, the solvent passes over the solute and system of solvent-solute reaches equilibrium. [*Sparks et al., 2007*]. The static method involves only static contact solvent with solute until equilibrium is reached. The equilibrium can be reached for binary, ternary or multi-compound liquid systems using both techniques.

As was mentioned before, TQ can be extracted from black cumin raw oil, that means TQ in the natural source is dissolved in the multi-component oil fraction. The artificial mixtures of TQ and refined rapeseed oil were used to simulate volatile oil of the black cumin.

In this paper results of solubility measurement with dynamic and static methods are presented for the thymoquinone and supercritical carbone dioxide.

Materials and methods

Materials

Pure CO_2 (99.9%) was purchased from Air-Liquid delivered at pressure up to 60 bar. Thymoquinone (TQ) purchased from Aldrich ($C_{10}H_{12}O_2$, purity 99%, 274666, Germany) was used without further purification. Commercial rapeseed refined oil from *ZPT Kruszwica*, Poland was used without any further purification.

Dynamic equilibrium apparatus

A flow-type apparatus were used for dynamic solubility measurements. Detailed description of apparatus was presented earlier [*Gurgenova et al., 2010*]. It is used for extraction and fractionation studies. The apparatus consists of column with initial volume $V = 56{,}5$ mL, designed to withstand maximum internal pressure of up to 300 bar at 60°C. The liquid CO_2 from a tank was first cooled with a cooling bath and liquefied, and then it was pumped with a high-pressure pump Jasco PU2080. The system has been filled with CO_2 and waited until the temperature and pressure of the system reached the desired value. Then model mixture were fed in the column. The mobile phase consisted of a mixture of refined oil and TQ, in which solvent is saturated by the solute as it flows countercurrent with feed flow through the column at predetermined constant flow rate. Steady flow were reached after half an hour. After few hours when the response of the TQ fraction was stabile on detector, it was assumed that equilibrium was reached and the measured concentration was recorded. Each of the experiments lasted from 10 to 12 hours, all collected products were weighted at the analytical balance. The concentration of TQ at the outlet was traced on-line. Analysis of the solubility values were carried out on a UV/VIS high-pressure detector *Jasco UV 970M* and *Borwin chromatographic software*. The profiles were recorded at following wavelengths: 255 nm, 260 nm, 265 nm simultaneously, as absorption by the solute is at its maximum at this wavelength [*Gorner, 2004*].

Concentration were calculated from the chromatograms using calibration curves, because the peak areas of the components calculated are related to their amount.

Static equilibrium apparatus

Installation for static solubility measurements for multi-component liquid system was built in our laboratory. Apparatus consists of viewing cell, with sapphire glass, volume of cell is about 55 ml. The liquid CO_2 from a tank was first cooled with a cooling bath and liquefied, and then it was pumped with a high-pressure pump *Jasco PU2080*. The upper phase was withdrawn from the cell by high-pressure piston *Waters M510* pump and fed to the bottom of the cell via UV-VIS detector *Jasco UV970M*, which measures amount of volatile fractions in the upper phase of the cell.

Results and discussion

Dynamic solubility

In the present work, the search for saturation curve was performed at a pressure of 120 bar and a temperature of 38 °C. At those conditions the solubility of black cumin oil is very low [*Fullana at el., 1999*], but the solubility of TQ is expected to be high. The supercritical carbone dioxide solubilities of TQ values are reported in Table 1.

Tab. 1.Experimental data

	Solvent	Feed				Extract	
Exp №	S_{CO2} ml/min	S^*_{feed} ml/min	$c_{feed\,TQ}$ w/w%	S_{TQ} g TQ/min	V_{feed} ml	m_{TQ} g	$c_{ext\,TQ}$ w/w%
1	1.8	0.368	0.1015	0.0406	39	0.0040	0.0013
2	1.8	0.331		0.0365	70	0.0071	0.0011
3	1.8	0.290		0.0320	44	0.0045	0.0009
4	1.8	0.462		0.0510	43	0.0044	0.0013
5	2.0	0.373	0.203	0.0823	56	0.0057	0.0025
6	1.8	0.100		0.0221	28	0.0028	0.0026
7	1.8	0.100		0.0221	22	0.0022	0.0025
8	1.8	0.333		0.0735	34	0.0035	0.0026
9	1.8	0.331	0.3045	0.1096	17	0.0017	0.0028
10	1.8	0.290		0.0960	57	0.0058	0.0027
11	1.8	0.462		0.1529	48	0.0049	0.0028
12	1.8	0.433		0.1433	41	0.0042	0.0028
13	2.0	0.121	0.406	0.0534	20	0.0020	0.0033
14	2.0	0.147		0.0649	19	0.0019	0.0035
15	2.0	0.356		0.1571	44	0.0045	0.0035
16	1.8	0.335		0.1478	46	0.0047	0.0032
17	1.8	0.355		0.1567	64	0.0065	0.0035
18	1.8	0.373		0.1646	38	0.0039	0.0035
19	1.8	0.333		0.1470	44	0.0045	0.0034
20	1.8	0.357		0.1576	49	0.0050	0.0034
21	1.8	0.368		0.1624	55	0.0056	0.0034
22	1.8	0.462		0.2039	49	0.0050	0.0034

$d_{oil} = 0.920$ [g/ml]

where: S_{CO2} – solvent flow rate [ml/min], S^*_{feed} – feed flow rate [ml/min], S_c – mass of TQ in the flow per minute [g TQ/min]; V_{feed} – volume of feed [ml]; m_{TQ} – mass of TQ in the extract [g]; $c_{feed\,TQ}$ – concentration of thymoquinone in the feed, [w/w%]; $c_{ext\,TQ}$ – concentration of thymoquinone in the extract, w/w%. Due to lower compressibility of rapeseed oil [*Rostocki at el., 2009*] density of used refined oil of 0.920 g/mL was constant during experiments.

The solvent flow rates were chosen to reach saturation condition according to the methodology of solubility measurement. At higher solvent flow rates, the contact time between the solvent and the solute has been shorter than the time necessary to saturate the solvent, and thus the mass ratio of solute at the column outlet have been smaller than the saturation value.

Additional flow parameter were introduced, as a mass of thymoquinone in the oil flowing through apparatus during process per minute:

$$S_{TQ} = S^{*}_{feed}\, c_{feedTD}\, d_{oil} \quad (1)$$

Due to complexity of experimental apparatus the range of CO_2 flow rates varied from 1.8 to 2 mL/min, but oil flow rates used to varied the most from 0.096 to 0.462 mL/min. Fig. 1. shows the effect of the TQ feed flow rate (S_{TQ}) on measured TQ concentration in the extract.

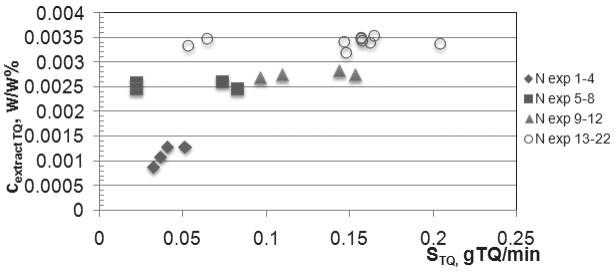

Fig. 1. The effect of the TQ feed flow rate on measured TQ concentration in the extract at P = 120 bar, T = 38°C

The absorption by the solute is at its maximum at wavelength of 260 nm. Fig. 2 presents the trends of weight concentration of TQ in the extract on input weight concentration of TQ in the feed at 260 nm wavelength at P = 120 bar, T = 38°C.

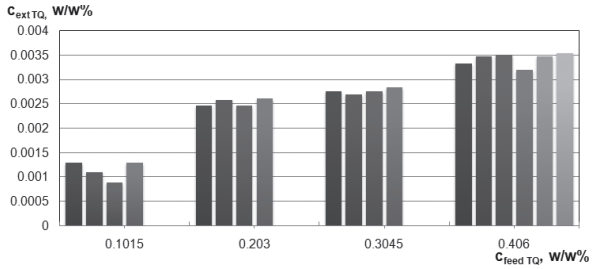

Fig. 2.The dependency of weight concentration of TQ in the extract on input weight concentration of TQ in the feed at 260 nm wavelength at P = 120 bar, T = 38°C

From the dependency of weight concentration of TQ in the extract on input weight concentration of TQ in the feed was found that solution reaches saturation state at P = 120 bar, T = 38°C completely independent of feed flow rate, taking into account that solvent flow rate is almost constant.

Static solubility

Each reported data (Tab. 2) is the average of at least three replicate samples.

Tab. 2. Solubility of thymoquinone in supercritical CO_2

Pressure (bar)	Solubility of thymoquinone (mole solute/mole CO_2)	Standard deviation (mole solute/mole CO_2)
Temperature = 28°C		
100	3.31E−05	±1.97E−06
120	6.94E−06	±5.87E−07
Temperature = 38°C		
100	2.39E−05	±4.48E−06
120	5.40E−05	±1.44E−05

The mole fraction solubilities of the solutes show a maximum relative standard deviation of 7.8% for thymoquinone solubilities which indicate the reliability and reasonability of the used method in measuring solubility of volatiles in supercritical CO_2. At the calculations solubility of refined oil was neglected, because at given conditions refined oil almost insoluble in CO_2 [*Gracia at el., 2009*].

To our knowledge, there is no previous reported solubility data for thymoquinone in supercritical CO_2. The experimental thymoquinone solubility data in SC-CO_2 at different pressures and temperatures are given in Table 2. and shown in Fig. 3 as well. The effect of pressure and temperature on the solubility indicates expected trends.

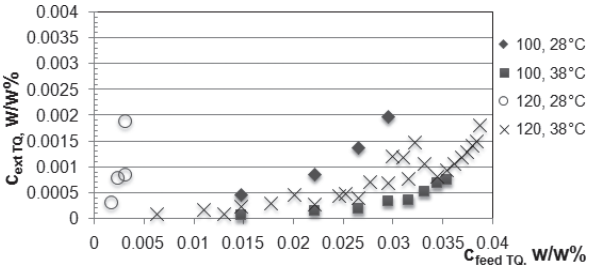

Fig. 3. Thymoquinone solubility at different pressures and temperatures

An increase in the operating pressure from 100 to 120 bar at the temperatures of 38°C resulted in an increase in thymoquinone solubility because of increasing the supercritical carbon dioxide density which leads to an increase in the solvating power of supercritical carbon dioxide and reduction in the (increasing the interactions between the thymoquinone and CO_2 molecules).

Conclusions

In the present study, a static and dynamic methods were applied to measure the solubility of thymoquinone in supercritical carbon dioxide. The solubility of thymoquinone was measured at pressures (100 and 120 bar) and temperatures (28 and 38°). For the dynamic experiments the saturation curve was founded, where TQ concentration for given feed TQ concentration was flow independent. The observed solubility for thymoquinone at the static experiments ranged from $6.94 \cdot 10^{-6}$ to $5.40 \cdot 10^{-5}$ (mole fraction).

The obtained results show that the solubility of thymoquinone increases as the pressure increases at each isotherm. But about the effect of temperature, there were different trends which show a rather sharp transition pressure of the CO_2-thymoquinone-refined oil system around the pressure of 120 bar.

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