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An experimental investigation into the solubility of *Moringa oleifera* oil in supercritical carbon dioxide

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ABSTRACT

The solubility of *Moringa oleifera* oil in supercritical CO_2 was investigated using a laboratory scale supercritical fluid extraction system operating at temperatures from 333 K to 373 K and pressures from 20 to 50 MPa. The oil solubility was found to be between 0.64 and 12.68 (g/kg CO_2). The results showed that the solubility increased with increasing pressure under isothermal conditions. However, the effect of temperature showed different trends depending on the pressures. To generalise the experimental results, four models were employed to correlate the solubility data, including the Peng–Robinson equation of state and three density based models, namely, the Chrastil, del Valle and Aguilera, Adachi and Lu models. While all four models correlated the experimental data very well, the del Valle and Aguilera model showed the best fit. The Peng–Robinson equation of state enabled a thermodynamic explanation of the observed experimental trends of the variations in the *M. oleifera* oil solubility in supercritical CO_2.

1. Introduction

Moringa oleifera is a very important tropical tree as most of its parts such as leaves, flowers, fruits, and immature pods have been traditionally used as highly nutritive vegetables in many countries (Anwar and Bhanger, 2003). The seeds of *M. oleifera* are a good source of oil. Depending on the variety, *M. oleifera* seeds contain between 33% and 41% oil which is sometimes known as "Ben oil". This oil has been used in the manufacture of perfume and hair care products, as lubricant in watch making and precision equipment, and as coagulation for water purification and as medicine for enhancing cardiac function (Anwar and Bhanger, 2003). Besides, the oil can also be used for edible purposes and is considered to be equivalent to olive oil in terms of its fatty acid composition (Abdulkarim et al., 2005).

Vegetable oil is commonly obtained by mechanical pressing and solvent extraction using organic solvents such as hexane. However, pressing gives relatively low yields, while the solvents used for extraction are often harmful to human health and the environment. Supercritical carbon dioxide is an inexpensive, non-flammable and non-toxic solvent and, for these reasons, the supercritical fluid extraction (SFE) technique using supercritical CO_2 is considered to be an attractive alternative to these conventional extraction methods (Smith et al., 2003). SFE has been extensively used in many processes, such as in food, pharmaceutical, biochemical industries, polymer processing and environmentally friendly chemical processing (Mustafa and Turner, 2011; Zaidul et al., 2007).

The extraction rate from solid materials such as seeds is often limited by the solubility of the oil in the supercritical CO_2. SFE process optimisation requires the knowledge of the solubility data, which allows the selection of the most adequate operating conditions, such as temperature, pressure, extraction time and solvent flow rate (Danielski et al., 2007b). Besides, the solubility information is important for the process design as well as analytical applications. Oil solubility can be measured using either static or dynamic method, both by contacting CO_2 with the previously obtained oil directly or with the ground substrate materials (Sovová et al., 2001). In the dynamic method, the supercritical fluid flows continuously through an equilibrium vessel containing the oil being studied or with a solid material of large surface wetted with the oil. The operation conditions are chosen so that the outlet stream can be assumed to have reached the equilibrium. The dissolved or extracted oil is usually precipitated out and weighed, and the gaseous flow exiting the restrictor is measured by using a wet or dry flow metre to determine the amount of the supercritical fluid used to dissolve the oil (del Valle and de la Fuente, 2006). A lot of researchers have used the dynamic method to investigate the solubility of different oils in supercritical carbon dioxide, such as sunflower oil (Soares et al., 2007), corn oil (Soares et al., 2007), rosehip oil (Machmudah et al., 2007), borage oil (Gaspar et al., 2002).

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In the static method, on the other hand, the oil and SC–CO_2 are contacted in a high pressure vessel and allowed to reach equilibrium under controlled pressure and temperature. The samples from both the vapour phase and the liquid phase are withdrawn and analysed. Both the dynamic and static methods have been applied to measure the solubility of oil in supercritical CO_2 (del Valle and de la Fuente, 2006).

As sometimes it is difficult and expensive to obtain equilibrium data at high pressures and temperatures, correlations and predictive modelling of solute solubility in supercritical CO_2 are essential. Different equations have been developed for mathematical modelling of solubility data in supercritical CO_2, such as theoretical equations of state (EoS) and semi-empirical correlation equations. The equations of state models have proven to be useful tools for the correlation of experimental data and prediction of the phase equilibrium. The Peng–Robinson equation of state with the van der Walls mixing rule has been shown to give good results for the description of the vapour-liquid equilibrium of complex mixtures with supercritical CO_2 (Setianto et al., 2009). Rodrigues et al. (2005) have successfully used the Peng–Robinson equation to describe the solubility of Brazil nut oil in supercritical CO_2. The phase equilibrium of Sacha Inchi oil in supercritical CO_2 has also been studied and correlated with the Peng–Robinson equation of state by do Prado et al. (2011). On the other hand, the density-based models provide very simple and efficient means to correlate the solubility of substances in a wide range of temperatures and pressures; they only use readily available independent variables (pressure, temperature and density of pure SC–CO_2). These equations include three or more parameters that are obtained on the basis of simple error minimisation using data fitting (Hezave et al., 2012). By far and large, numerous studies have been performed to investigate and predict the solubility of oil in supercritical CO_2 using the density based models (Chen et al., 2011; Sovová et al., 2001).

The aim of this study was to experimentally obtain the solubility data of *M. oleifera* oil in supercritical CO_2 in a pressure range between 20 and 50 MPa and at temperatures of 333 K, 353 K and 373 K. The experimental solubility data were analysed using the Peng–Robinson equation of state with the conventional van del Waals mixing rules. Three density based models, proposed by Chrastil (1982), del Valle and Aguilera (1988), and Adachi and Lu (1983) were also used to correlate the solubility data in this study.

2. Experimental procedures

2.1. Materials

The *M. oleifera* seeds used in this work were provided by Department of Agriculture and Food of Western Australia. Prior to processing, the samples were dried at 50 °C in air in an electrically heated oven for 8 h and then ground using a Waring blender (model W-800S, Waring, Torrington, CT). The ground samples were then sieved with a sieved shaker (model EFL2000/2, Endecotts Ltd., London, England). The final *M. oleifera* seed samples were less than 1 mm and had moisture content of 4.6%. The samples were sealed in plastic bags and kept in darkness in a refrigerator till the time of experimentation.

2.2. Apparatus

The SFE extraction experiments were carried out using a SFT Custom SCW-SFE system (Newark, DE, USA) as schematically shown in Fig. 1. Liquid CO_2 was supplied from a CO_2 cylinder through a siphon tube and then introduced into the system through a dual piston pump. The pump was designed to be capable of operating at pressures up to 68 MPa. The CO_2 fluid was heated to its supercritical status through a preheater and a heating jacket around the vessels. A robust variable restrictor valve was used to control the flow rate. In order to prevent sample plugging, the restrictor was warmed electrically. A flow metre was provided to indicate the flow rate of CO_2 being passed through the system. The supercritical CO_2 with dissolved compounds passed through a heated restrictor and was subsequently expanded to ambient pressure. The extract was precipitated in a collection vial at ambient pressure and temperature. A volume totalizer (Model 33400-58 Cole Parmer Instrument Company, Vernon Hills, IL, USA) was used to measure the total volume of CO_2 used in the extraction.

The experimental values of the solubility were obtained with the dynamic method. The dynamic method is based on the assumption that the solute–solvent system reaches equilibrium as the solvent flows over the solute, usually achieved at a relatively low flow rate of the solvent, determined by trial-and-error in experimentation as discussed in Section 3.2 below. Solubility measurements were carried out at temperatures 333, 353, 373 K and pressures 20, 30, 40, 50 MPa. The flow rate of CO_2 was kept at 3.68 g/min. In each experiment, approximately 10 g of a *M. oleifera* seed sample was loaded into the 50 ml supercritical CO_2 vessel and the remaining volume was filled with glass wool at the bottom and top of the vessel. The extract was collected into a previously weighted glass vial at every 5–30 min for 4 h, and weighted immediately after the collection. Each experiment was repeated three times to assure statistically valid results. The experimental results presented in this study were the average of three measurements under the same conditions, with error bars showing the standard deviations of these measurements. The effects of pressure and temperature on the solubility of *M. oleifera* oil in supercritical carbon dioxide were analysed by the two-way repeated analysis of variance (ANOVA). Values of $p < 0.05$ were regarded as significant, in accordance with Zaidul et al. (2007), Machmudah et al. (2007) and Nguyen et al. (2011).

2.3. Solubility calculation

Normally an extraction curve is divided into three stages (Min et al., 2010). In the first stage, the yield of the extract increases rapidly and linearly with solvent consumption or extraction time and then enters into a slowly declining second stage. In the third stage, the extraction yield remains almost invariant, indicating the completion of extraction process. According to Reverchon and Marrone (2001), the solubility can be calculated from the experimental plot of the oil yield as a function of the mass flow rate of the solvent. Accordingly, the solubility of *M. oleifera* oil in supercritical CO_2 was determined from the slope of the linear part of extraction curve in this work, as described by the following equation:

$$S = \frac{\text{mass of oil}}{\text{volume of supercritical carbondioxide}} \quad (1)$$

where S is the solubility of *M. oleifera* oil in supercritical CO_2

2.4. Determination of fatty acid composition of M. oleifera oil

Fatty acid methyl esters were prepared according to the standard IUPAC method 2.301 (IUPAC, 1987). 0.25 g of an extracted oil sample was mixed with 6 ml of 0.5 N methanol sodium hydroxide solution and brought to reflux in a water bath at 90 °C for 30 min to facilitate complete saponification of the oil. 7 ml of the BF_3-CH_3OH solution was then added and continuously boiled for another 5 min to promote the formation of methyl ester. Then, the mixture was cooled to room temperature and 5 ml of heptane