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Solubility of grape seed oil in supercritical CO_2: Experiments and modeling

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ABSTRACT

The solubility of grape (*Vitis vinifera* L.) seed oil in supercritical CO_2 was measured in the temperature range 313–343 K and pressure range 20–50 MPa using the dynamic technique. Several data and global trends were reported. The results show that, at constant temperature, the solubility increases with the increase in pressure, while the effect of the temperature is different for low and high pressure. The experimental data were modeled by eight density-based models and a thermodynamic model based on the Peng-Robinson equation of state. By best fitting procedures, the "free parameters" of the various models were calculated: in general, all the tested models have proved to be able to predict the solubility of grape seed oil in supercritical CO_2. Differences in model capabilities have been discussed based on the main characteristics of the various models, evidencing their distinct and common features. The predictive capability of the thermodynamic model was comparable to that of the density-based models.

1. Introduction

Grape seeds are a by-product of the wine-making process; they contain between 4% and 17% oil [1,2]. Grape seed oil consists mainly of triacylglycerols, with minor amounts of 1,2 diacylglycerols and oxidized lipids [2]. The major fatty acids of grape seed oil are linoleic acid (C18:2 ≈70%), oleic acid (C18:1 ≈15%), palmitic acid (C16:0 ≈7%) and stearic acid (C18:0 ≈3%) [1–3]. Grape seed oil is a noble source of vitamin E, with substantial amounts of tocopherols and tocotrienols [1,2], and exhibits high antioxidant activities which make it increasingly attractive in culinary, cosmetics, pharmaceutical and medical applications [1,4,5].

Supercritical fluids (especially CO_2) are receiving a central attention as future industrial solvents, particularly in the field of high value-added products and applications. Supercritical fluids possess gas-like viscosity and diffusivity, and liquid-like density and solvating power [6]. When used as solvents, they can be easily separated from the extracted product by simple depressurization. Besides, the thermodynamic properties of supercritical fluids can be easily tuned by adjusting the operating conditions. Supercritical CO_2 (SC-CO_2), in addition to the advantages mentioned above, presents other obvious strengths: non-toxicity, non-flammability, and low-cost.

The solvent power of SC-CO_2 depends essentially on the nature of the solute and the system pressure and temperature. An effective design and scale-up of supercritical fluids processes, such as supercritical fluid extraction and fractionation, require the knowledge of the thermodynamics of the system, *i.e.* the phase equilibria [7]. Thus, the determination of the solubility of a substance in the supercritical phase is the first step in the development and evaluation of any supercritical process, and it is also mandatory for establishing the optimal operating conditions [8–11].

The experimental determination of the solubility in supercritical fluids is generally accomplished through two approaches in the literature, the so-called static and dynamic methods. In the static method, solute and solvent are placed within a fixed volume vessel, which is stirred mechanically or by recirculating the vapor phase until equilibrium is established. In the dynamic method, a continuous apparatus is used to contact the two phases and the composition of the stream leaving the apparatus is determined after expansion and separation of the solute from the supercritical solvent [8,12]. Significant research works were published in the past two decades focused on the determination of solubility of various organic compounds in SC-CO_2, such as drugs [10,13,14], seed oils [15–17], pollutants [18], dyes [19–21], food colorants [22], polyphenolic compounds [23] CO_2-philic compounds [24] and many more. However, the solubility data reported in the literatures are often extremely divergent and inconclusive.

In this work, the dynamic method was used to experimentally determine the solubility of grape seed oil in SC-CO_2 in the range

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of pressure and temperature of practical importance (between 20 and 50 MPa and between 313 and 343 K). It is worth highlighting that only a limited number of literature reports are available which deal with solubility of grape seed oil; in addition, they experimentally investigated the solubility in restricted ranges of pressure and temperature.

The bulk majority of the scientific papers determine the solubility of solutes in SC-CO_2 through theoretical models. Therefore, testing the predictive power of solubility models commonly used in the literature taking as a reference a common and extended basis of experimental data is of extreme importance. In this regard, the experimental data were modeled using eight density-based models and a thermodynamic model based on Peng-Robinson Equation of State (EoS). The models are compared and discussed in terms of their effectiveness in predicting the experimental data.

2. Experimental

2.1. Materials, equipment and extraction procedure

CO_2 (4.0 type, purity greater than 99.99%) purchased from Messer (Padua, Italy) was used as supercritical solvent. Dry grape seeds (humidity 1–2%) of Moscato cultivar were milled by a grinder (Sunbeam Osterizer blender, Boca Raton, USA) and extracted using the supercritical equipment (PRORAS, Rome, Italy) as detailed in [4] at a pressure of 50 MPa and a temperature of 323 K. A minor modification was made by adding a mini Cori-Flow digital mass flow meter (Bronkhorst, Ruurlo, The Netherlands) placed on the liquid CO_2 line, upstream of the CO_2 pump, as discussed in [2]. The extracted grape seed oil was stored at ambient temperature in tightly closed dark glass vials sealed with Parafilm before being used in the solubility determination tests. Lipids composition of Moscato grape seed oil as established by ^{1}H NMR quantitative analysis resulted the following (data in mole fraction ± SD): triacylglycerols: 0.982 ± 0.005; diacylglycerols: 0.0110 ± 0.0003; sterols: 0.0050 ± 0.0002; oxidized lipids: 0.0020 ± 0.0003 [2]. Fatty acid composition of Moscato grape seed oil is reported in Table 1 [2]. The major triacylglycerols found were: PLL (16:0,18:2,18:2), POL (16:0,18:1,18:2), POO (16:0,18:1,18:1), LLL (18:2,18:2,18:2), OLL (18:1,18:2,18:2), OOL (18:1,18:1,18:2), and finally OOO (18:1,18:1,18:1) [2].

2.2. Solubility determination procedure

The solubility of grape seed oil at different temperatures and pressures was determined by thoroughly mixing 5 g of oil with 145 g of glass beads (diameter: 1.05 mm) in an extractor of 0.1 L volume (extractor assembly reported in [25]) and re-extracting the oil by SC-CO_2. The amount of oil used in the experiments (5 g) was fixed to allow a significant wetting of the glass beads, but avoiding that the oil came down along the cylindrical extractor by gravity, which would compromise the reliability of the solubility data, as evidenced by Sovovà et al. [8] (see Section 4.1. for details).

The pressure and temperature were controlled during the tests with an accuracy of ±0.1 MPa and ±1 K, respectively. The cumulative CO_2 consumption during the tests was measured and recorded by the digital mass flow meter. The extracted oil dropped down in a beaker placed over a precision balance (Mettler Toledo PL-203-S, Milan, Italy) and its amount was recorded during the tests. The range of flow rates required to saturate the solvent was established by conducting several tests at the same pressure and temperature and varying the solvent flow rate (see Section 4.1).

The solubility data for a given pressure and temperature was calculated as the initial slope of the plot where the amount of extracted oil (y-axis) was plotted against the CO_2 consumed (x-axis).

As a general rule, the static method is preferable with respect to the dynamic method for measuring the solubility of a liquid consisting of a mixture of components. Actually, in the dynamic method differences in composition of the solute saturating the solvent will occur during the course of the dynamic test. Made this premise, in the present case the use of the dynamic method seems adequate: the oil consists of 98.2% triacylglycerols (and 1.1% diacylglycerols), so that the presence of the other minor constituents should not affect to an appreciable extent the value measured at the beginning of the dynamic test and assumed as the solubility value of grape seed oil in SC-CO_2.

3. Modeling

The modeling of solubility in SC-CO_2 generally follows two approaches: one option is resorting to density-based correlations; another is using thermodynamic models based on EoS. The models were fit to the experimental data using MATLAB R2014a by nonlinear optimization function *lsqcurvefit*. The deviation between model prediction and experimental data was quantified using root mean square error (RMSE) and percent average absolute relative deviation (AARD).

3.1. Density-based models

In the scientific literature, there are at least three broad categories of density-based models.

The first group includes those models that are based on the law of mass action applied to a solvation reaction. Notable examples in this group are the Chrastil's model [26] and its modifications which foresee a linear relationship between the logarithm of solubility and the logarithm of solvent density. Some of the important modifications comprise the models by Adachi and Lu [27], del Valle and Aguilera [28], and Sparks et al. [29].

The second category consists of those models that are based on the theory of dilute solutions. This group of models assumes an isofugacity condition between the solute in the condensed phase and the solute solubilized in the supercritical phase. Such group includes the models by Kumar and Johnston [30], Bartle et al. [31], and Mendez-Santiago and Teja [32].

The third group contains models which are purely empirical in nature and which correlate the solubility with pressure and temperature simply by using polynomial functions. An important example of this last class is the Yu et al.'s model [33] which has several modifications in the literature.

The model developed by Chrastil [26] is derived based on the association reaction between solute and solvent. It is assumed that, at equilibrium, one molecule of solute A associates with k molecules of solvent B, to form a solute–solvent complex. The final expression of the solubility S (kg m^{-3}) in the supercritical phase is given by Eq. (1):

Table 1
Fatty acid composition (% of total fatty acids) from FAME GC-FID-MS analysis of Moscato grape seed oil. Data are expressed as mean ± SD. Data from Fiori et al. [2].

C14:0	C16:0	C17:0	C18:0	C18:1 (ω-9)	C18:2 (ω-6)	C18:3 (ω-3)	C20:0	C20:1 (ω-9)	C20:2 (ω-6)
0.051 ± 0.003	8.89 ± 0.21	0.049 ± 0.001	2.84 ± 0.02	15.3 ± 0.1	71.0 ± 0.3	0.46 ± 0.01	0.14 ± 0.01	0.11 ± 0.01	0.041 ± 0.010