Squalene Solubility On Sc-Co_2 : New Experimental Data And Modelling

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ABSTRACT

The solubility of squalene in supercritical carbon dioxide (SC-CO_2) was measured at temperatures of 40°C and 50°C and pressures of 20, 30 and 40 MPa, and at 60°C and 20 MPa. Experimental SC-$C0_2$ solubility data were collected from the literature, and analyzed together with the values obtained in this work. The values were correlated by the equation of Chrastil and modeling with Peng-Robinson equation of state with classic mixture rule and group contribution equation of state (GC-EOS, Skjold-Jørgensen -1984). All experiments were done in triplicate and conducted with an equilibrium time of 3 hours, and the solubility data obtained in this work agreed in order of magnitude with literature data. The crossover point was at 25 MPa, condition where the solubility is independent of temperature. Thermodynamic modeling showed that Peng-Robinson equation of state was successful for searching binary interaction parameters to fitting experimental data reported in this work, this model was strongly influenced by the value of critical constants for squalene. The GC EOS model predicted the behavior of experimental data up to 20 MPa, his performance was influenced by the parameters groups, binary interaction and strongly by the value of critical hard-sphere diameter of the squalene.

Key-words: squalene, solubility, supercritical, modelling.

INTRODUCTION

For supercritical technology, the extraction curves and phase equilibrium data under different operational conditions of temperature and pressure are very useful for process optimization, and the thermodynamic modeling of phase equilibrium at high pressures is a powerful auxiliary tool. Values for the solubility of solutes obtained from natural products in SC-CO_2 are data of great importance in the evaluation of systems of interest, since they provide information about the influence of pressure and temperature on the solubility and are useful to obtain the binary interaction parameters in thermodynamic modeling.

Squalene ($C_{30}H_{50}$), is a solute of interest in the extraction and fractionation with SC-CO_2, since it is a hydrocarbon with an extremely unsaturated linear chain and is heat unstable and light sensitive. It represents 50 to 70% by mass of some fish oils, such as shark oil (*Centrophorus squamosus*) and in lower concentrations in some vegetable sources, such as rice, corn, peanut and amaranth oils. The effect of olive oil in reducing the risk of cancer is attributed to the presence of squalene. Properties include antioxidant activity due to its unsaturated chain implicated in its oxidative instability, increasing longevity and strengthening the immunological system and also being an anti-carcinogenic agent [1], reducer of cholesterol levels [2].

1. MATERIALS AND METHODS

The CO_2 (99.5% pure) was purshased from *White* Martins Gases Industriais (Campinas, Brazil). Squalene (Fluka Chemie, gas chromatography grade, purity ≥ 97.0%) was purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA).

Solubility procedures

The experimental values were obtained by the static method, whose methodology has been discussed in detail elsewhere [3]. The experimental conditions included temperatures of 313 K and 323 K and pressures of 200, 300 and 400 bar, and also at 333 K and 200 bar. The experiments were carried out in triplicate with an equilibrium time of 3 hour and employing n-hexane to clean the collector. The solvent was evaporated off in a vacuum oven at 333 K to obtain dry squalene. The values for solubility were calculated as the ratio of the total mass of extracted squalene (extraction + cleaning process) to the CO_2 mass in the collector.

Values for the density of CO_2 under the different conditions of temperature and pressure were calculated using a computer program that employed the empirical equation of Huang et al. [4], which reproduces the experimental values of IUPAC [5].

Data analysis

Obtained solubility data were correlated using Chrastil equation [6], which can be expressed as a mass fraction as follows:

$$\ln\left(\overline{Y}\right) = (k-1)\ln\rho + \frac{a}{T} + b \qquad (1)$$

where $\bar{Y}$ is the solubility (kg/kg CO_2).

Modelling solubility data was firstly using Peng-Robinson cubic equation of state [7]:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \quad (2)$$

The mixing rule of Van der Walls was used, with Ka_{ij} and "Kb_{ij} as binary interaction parameters, computed by fitting experimental vapor-liquid equilibrium data to the model equation. In this case Tc=782.129K , Tc=11.121 bar, and ω = 1.9083 [8] were used.

The Group Contribution Equation of State [9] (GC-EOS) was too used for modelling, in this equation the residual Helmholtz energy is described by a free volume term (repulsive contribution) expression for hard spheres with a contribution from attractive intermolecular forces:

$$A^R = A^R_{fv} + A^R_{att} \quad (3)$$

For GC-EOS the group parameters (q_i, g^*_i, g'_i and g''_i) and binary interaction parameters (k'_{ij}, k^*_{ij} and α_{ij}) used were obtained from the literature ([10], [11], [12]). Thermophysical properties used were: Tc= 838.1 K, Pc= 6.5 bar e dc= 9,336. The GC-EOS calculations were performed using the GPEC software (www.gpec.plapiqui.edu.ar)

2. RESULTS AND DISCUSSION

The experimental values for the solubility of pure squalene in SC-CO_2 are presented in Figure 1 and they were compared to values measured at pressures of 100 to 250 bar by [13]. The linear relationship between the logarithm of the solubility (Y) and the logarithm of the SC-CO_2 density was obatined by Chrastil equation.

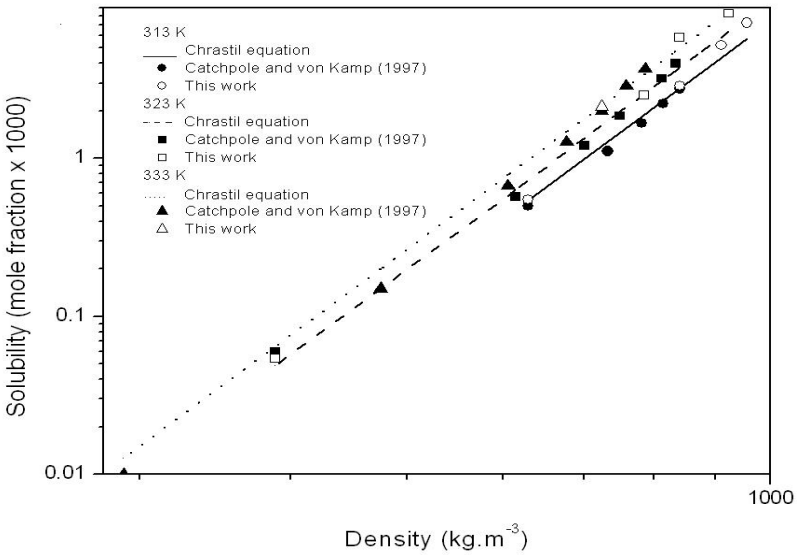

Figure 1. Comparison of the experimental data with those calculated from the Chrastil equation.

The Peng Robinson equation with the classic mixing rule was used to model the phase equilibrium. It was shown that in the majority of cases, binary interaction parameters that could correlate with the experimental data could not be found. Only when the critical properties and acentric factor reported by Ruivo et al. [8] were used, was this possible. In Figure 2, the experimental values for solubility are compared with the values obtained by thermodynamic modeling employing the Peng Robinson equation and the critical constants and acentric factor reported by Ruivo et al. [8].

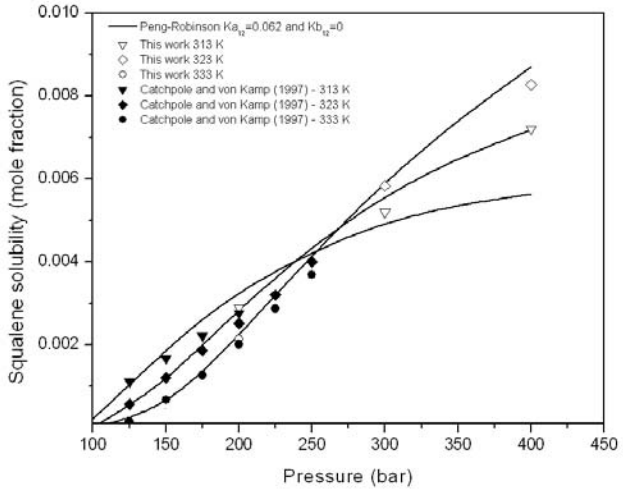

Figure 2. Comparison of the experimental data and those calculated from the thermodynamic model using the Peng-Robinson equation and the critical properties and acentric factor from Ruivo et al. [8]

The GC-EOS model can predict the behavior of the experimental data at a pressure of 200 bar. Above this value it predicts a solubility decrease (Figure 3).

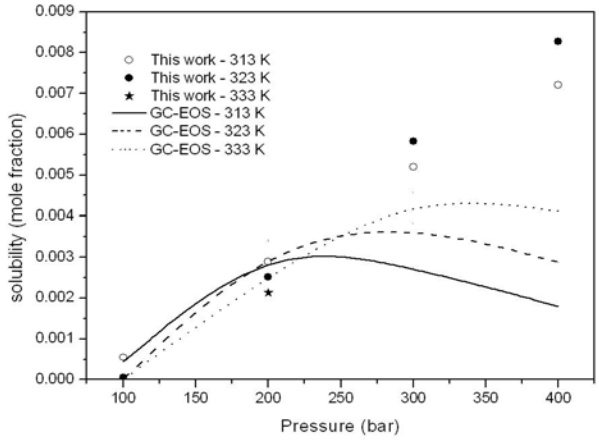

Figure 3. Solubility of squalene in SC-CO_2: Experimental data (○ ● ✶) and GC-EoS model (—, -----, …..), All calculations for squalene used: Tc= 838.1 K, Pc= 6.5 bar and dc= 9.336.

3. CONCLUSIONS

New data for squalene solubility in SC-CO2 was obtained, correlated using the Chrastil equation and modeled using the cubic equation (Peng -Robinson) and the group contribution equation (GC EOS). The results showed that modeling with the Peng-Robinson equation of state was successful fitting the experimental data reported. The GC-EOS model predictes the behavior of the experimental data up to 200 bar and by the value of the critical hard sphere diameter of the squalene.

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