PHASE BEHAVIOR DATA AND THERMODYNAMIC MODELING OF THE BINARY SYSTEM {CO$_2$ + COUMARIN} AT HIGH PRESSURES

Jessica C. Lima[1], Jonas M. Jaski[2], Vladimir F. Cabral[1], Carla C. R S. Rossi[1],
Lisiane dos S. Freitas[3], Lúcio Cardozo-Filho[1,2,4]*

[1] Universidade Estadual de Maringá, Departamento de Engenharia Química, Maringá, PR, Brasil. ORCID: 0000-0002-0017-9114;
ORCID: 0000-0002-5835-9249; ORCID: 0000-0003-3077-5811; E-mail: lucio.cardozo@gmail.com - ORCID: 0000-0002-1764-9979
[2] Universidade Estadual de Maringá, Departamento de Agronomia, Maringá, PR, Brasil. ORCID: 0000-0002-2454-3638
[3] Universidade Federal de Sergipe, Departamento de Química, São Cristovão, SE, Brasil.
[4] Centro Universitário Fundação de Ensino Octávio Bastos, Núcleo de Pesquisa, São João da Boa Vista, SP, Brasil.

Abstract - In this work, vapor - liquid (VLE) equilibrium for the binary system carbon dioxide (1) + coumarin (2) at high pressures was measured by a static synthetic method using a variable-volume view cell. Experimental data were obtained in the temperature range of 318 - 338 K and pressures up to 20 MPa. Coumarin molar fraction ranged from 3.0x10^{-3} to 6.0x10^{-3}. Coumarin melting point reduction at high pressures was observed. The experimental results were modeled using the Peng-Robinson (PR) equation of state with van der Waals quadratic mixing rules (vdW - QMRs), providing a good representation of the experimental phase equilibrium data. Critical properties and the acentric factor were estimated using the Constantinou and Gani method, which showed to be satisfactory on the quality of data correlation. Results indicate coumarin solubility increases with increasing phase transition pressure at a given temperature.
Keywords: Coumarin; CO$_2$; Phase transition; Experimental data; Peng-Robinson Cubic Equation.

INTRODUCTION

Coumarin and its derivatives belong to a large class of compounds that naturally contain benzo-α-pyrone. They are widely used as fragrance ingredients, fixing agents in cosmetics, dyes and aromatic compounds (Fylaktakidou et al, 2004; Matos et al, 2015; Symeonidis et al, 2009). Coumarin has various biological activities such as anti-inflammatory, antitumor, anti-allergic, anti-HIV, antiviral, antioxidant, antimicrobial, and anti-asthmatic (Borges et al, 2005; Matos et al, 2011; Matos et al, 2015; Tabart et al, 2009). Coumarin can be found in a wide variety of fungi, bacteria, plants, and essential oils (Hamdi et al, 2008; Matos et al, 2015; Panteleon et al, 2008).

Previous studies using supercritical carbon dioxide (scCO$_2$) and co-solvents to extract coumarin from natural sources are available (Lanças et al, 1997; Oliveira et al, 2013; Rodrigues et al, 2008; Vilegas et al, 1997). The use of scCO$_2$ for the extraction of coumarin and other bioactive compounds is an interesting technique because this fluid has unique characteristics that enable the extraction free of organic solvents.

Interaction between solvent and solute is important to develop the extraction of bioactive compounds, and other applications such as nanoencapsulation (Dohrn et al, 2010; Reverchon and De Marco, 2006). Solubility measurements of the system carbon dioxide and coumarin can contribute to optimize supercritical extraction, since the transfer mass coefficient has implicit dependence (Dohrn et al, 2010). The study of phase behavior provides important information about a system. Adjustment of mathematical models to experimental data allows the construction of a phase diagram.

* Corresponding author: Lúcio Cardozo-Filho - E-mail: lucio.cardozo@gmail.com

Coumarin solubility investigations by analytical or semi-continuous flow methods are available in the literature (Rodrigues et al, 2008; Yoo et al, 1997). In these methods, the composition varies throughout the experiment. However, data obtained by the static synthetic method with a view cell are unpublished. The main differential of this technique is the possibility to visualize and identify phase transition types. Phase transition measurements using the proposed static method are adequate to avoid supersaturation regions in opposition to the dynamic method.

Thus, this work focused on measuring and modeling phase equilibrium data of the binary system CO_2 (1) + coumarin (2) at high pressures and temperature range of 318 K-338 K. The static synthetic method with a variable-volume cell was used to determine phase transitions. Experimental data of phase equilibria were modeled by the Peng-Robinson cubic equation with van der Waals quadratic mixing rules. The coumarin mole fractions investigated varied from 3.0×10^{-3} to 6.0×10^{-3}. Vapor - liquid (VLE) phase transition type was observed.

MATERIALS AND METHODS

Materials

Carbon dioxide (CO_2) was purchased from White Martins S.A (Osasco-SP, Brazil) with purity of 99.9 wt% (liquid phase). Coumarin with 98% purity degree was acquired from Aldrich (São Paulo-SP, Brazil). All substances were used without any pre-treatment.

Apparatus and Experimental Procedure

The apparatus used in this work consisted of a high-pressure variable-volume cell, following the static synthetic method. Methodology and apparatus were described in previous works (Ferreira et al, 2013; Giufrida et al, 2014; Giufrida et al, 2016; Pinto et al, 2013; Zanette et al, 2014). Maximum internal volume of the equilibrium cell was 25 cm^3, internal cell diameter was 1.8 cm and contained a movable piston. It also had two sapphire windows, one for visual observations, 2.5 cm inner diameter (i.d.), and a lateral one for light entrance, 1.5 cm i.d. Maximum operating temperature and pressure were, respectively, 423 K and 35.0 MPa.

Figure 1 shows a schematic view of the experimental apparatus employed.

The experimental procedure is summarized as follows: a known amount of coumarin, determined on a precision scale balance (Marte, model AM220, Santa Rita do Sapucaí, MG, Brazil), was loaded into the equilibrium cell, with an uncertainty of ± 0.0001 g. The cell was then flushed with low pressure CO_2 to remove any residual air. The amount of CO_2 remaining in the equilibrium cell was negligible (~10^{-5} mol) when compared to the total amount of CO_2 used to determine experimental data. A given amount of CO_2 was loaded using a syringe pump (ISCO, model 500D, Lincoln, USA), resulting in an uncertainty of ±0.005 g in CO_2 loadings. The mixture was conducted under constant stirring using a magnetic bar inside the cell while obtaining experimental data.
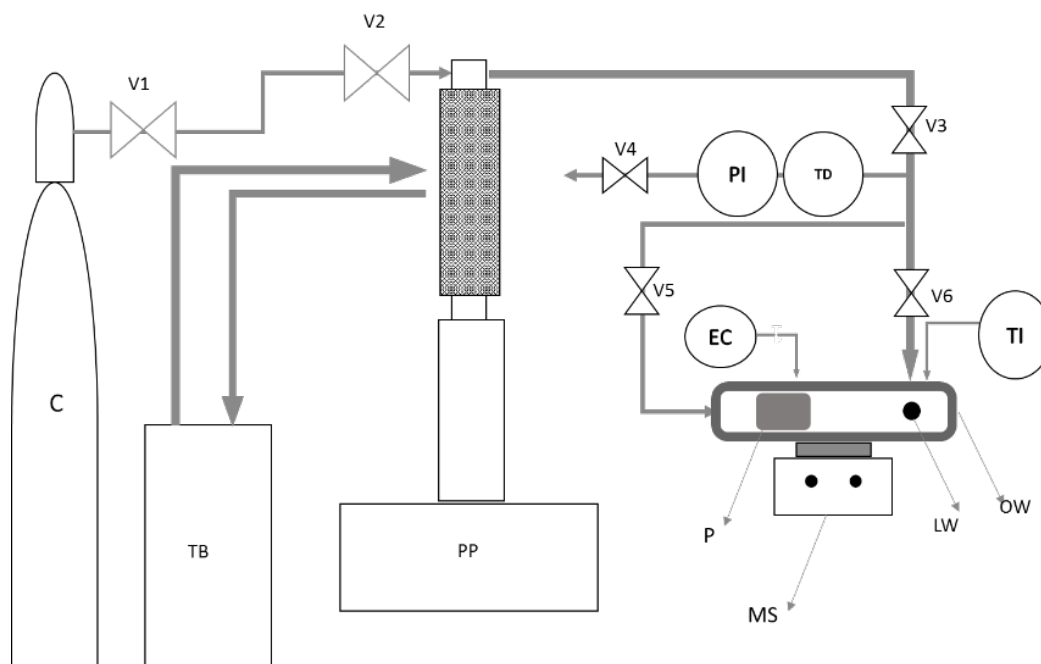
Figure 1. Schematic diagram of the experimental apparatus: (C) CO_2 cylinder; (V1, V2, V3, V4, V5, and V6) valves; (TD) pressure transducer; (PI) pressure indicator; (TI) temperature indicator; (OW) observation window; (LW) lighting window; (EC) equilibrium cell, stainless steel 25 cm^3 maximum capacity; (P) piston; (MS) magnetic stirrer; (PP) pressure control pump, and (TB) thermostatic bath.

The cell was equipped with an aluminum jacket for temperature control. A PID controller (DIGI MEC, SHM 112, Sertãozinho, SP, Brazil) was connected to a thermocouple (T type, uncertainty of ±1.0 K), which was fixed in direct contact with the mixture inside the cell.

CO_2 was used as an auxiliary fluid at the back of the cell to pressurize the system slowly until it reached a single phase. The system remained at this point for at least 30 min to guarantee stabilization in a homogeneous state. The pump was used in pressure gradient mode, with gradual decrease of pressure at 0.1 MPa.min^{-1}, until the phase transition was observed (Pinto et al, 2013).

The experiments were carried out in the temperature range of 318 K - 338 K. Phase transitions were determined visually, as described by McHugh and Krukonis (1994). Experiments were obtained in triplicate for all temperatures studied.

THERMODYNAMIC MODELING

The experimental data obtained in the present work were correlated using the Peng- Robinson equation of state. All transitions were considered vapor-liquid equilibria. The isofugacity criterion for each component i in the system was used in the calculations as follows:

$$y_i^{f1}\hat{\varphi}_i^{f1} = y_i^{f2}\hat{\varphi}_i^{f2} \tag{1}$$

where y_i^{f1} and y_i^{f2} are the mole fractions of component i in the fluid phases f^1 and f^2, respectively, φ_i^{f1} and φ_i^{f2} are the fugacity coefficients of component i in the same fluid phases. The van der Waals (vdW) quadratic mixing rules (QMRs) for a and b parameters were used in all calculations.

$$a = \sum_{i=1}^{c}\sum_{j=1}^{c} y_i y_j \sqrt{a_i a_j}(1 - k_{ij}) \tag{2}$$

$$b = \sum_{i=1}^{c}\sum_{j=1}^{c} y_i y_j \frac{b_i + b_j}{2}(1 - l_{ij}) \tag{3}$$

where y_i is the mole fraction of component i, a_i and b_i are the Peng-Robinson parameters for the pure component i, c is the number of components, and k_{ij} and l_{ij} are the binary interaction parameters.

Binary interaction parameters were fitted for each temperature (318, 328 and 338 K) using the experimental data of Table 1 and the objective function (Equation 4).

$$OF(P) = \sum_{o=1}^{no}(P_{exp} - P_{calc})^2 \tag{4}$$

Table 1. Experimental solubility. Phase equilibrium data for temperature (T), pressure (P) with standard deviation, and molar fraction x for the CO_2 (1) + coumarin (2) system.

Temperature/K^a	y₂ (coumarin)	Pressure/MPa	Transition
318	3.0x10⁻³	10.85±0.032	VLE
318	4.0x10⁻³	13.65±0.153	VLE
318	4.5x10⁻³	14.80±0.007	VLE
318	5.0x10⁻³	15.46±0.118	VLE
318	5.5x10⁻³	16.22±0.013	VLE
318	6.0x10⁻³	17.00±0.071	VLE
328	3.0x10⁻³	13.93±0.190	VLE
328	4.0x10⁻³	15.22±0.035	VLE
328	4.5x10⁻³	15.92±0.175	VLE
328	5.0x10⁻³	16.72±0.038	VLE
328	5.5x10⁻³	17.36±0.205	VLE
328	6.0x10⁻³	17.91±0.034	VLE
338	3.0x10⁻³	15.54±0.105	VLE
338	4.0x10⁻³	18.00±0.274	VLE
338	4.5x10⁻³	18.39±0.170	VLE
338	5.0x10⁻³	18.86±0.010	VLE
338	5.5x10⁻³	19.46±0.210	VLE
338	6.0x10⁻³	19.86±0.057	VLE

^{a}u(T) = 1.0 K

where no is the number of data points and P_{exp} and P_{calc} are, respectively, experimental and calculated pressure at the bubble point.

Previous work (Ferreira et al, 2013) conducted by our research group described the procedure to minimize the objective function. According to the authors, the "Solver" tool available in the Microsoft Excel (2016 version) spreadsheet for Windows and the XSEOS (Castier et al, 2008) Excel add-in were used to minimize the objective function and fit Peng-Robinson interaction parameters.

Critical temperature (T_c = 794.77 K), critical pressure (P_c = 4.347 MPa), and acentric factor (ω = 0.3945) of coumarin used in the PR-EoS were obtained using the Constantinou and Gani method (Poling et al, 2000). Similar values were found by Yoo et al. (1997) using the Lyderson-Forman-Thodos method. The values of same properties for CO_2 were obtained from Poling et al. (2000).

Absolute average deviations (AAD%) between calculated and experimental data were calculated according to equation (5)

$$AAD = \frac{1}{N}\left(\frac{|P_{cal} - P_{exp}|}{P_{exp}}\right)100 \tag{5}$$

where N is the number of experimental data points in an isothermal, P_{cal} (MPa) is the theoretically calculated transition pressure, and P_{exp} (MPa) is the experimental transition pressure.

## RESULTS AND DISCUSSIONS

Experimental Results

Table 1 shows experimental data of phase transitions for the binary system CO_2 (1) + coumarin (2). The measured experimental data are presented in terms of mole fraction of coumarin (2) and the transition pressure value.

Standard deviation for the pressure transition was calculated for triplicate values of the phase transition (MPa) in the range of 0.01 - 0.05 MPa based on three repetitions for each experimental point. Experimental conditions of pressure, temperature, and mole fraction of coumarin were 10 to 20 MPa, 318 to 338 K, and 3.0×10^{-3} to 6.0×10^{-3}, respectively.

The phenomenon of coumarin melting point reduction at high pressures has been discussed in a previous study (Rodrigues et al., 2008). This hypothesis was confirmed by visual method since the experimental apparatus used in the present work provided a clear view of phase transitions. Solubility of supercritical CO_2 inside the solid particle caused the melting point depression (Lian et al, 2010). Figure 2 shows the liquid coumarin formed at 318 K and in mole fraction of 6×10^{-3}, due to melting point depression at high pressure.

The experimental data of phase transition pressures reached values up to 20 MPa with 6×10^{-3} coumarin mole fraction. To reach a homogeneous phase, pressure higher than 30 MPa is required if the coumarin molar fraction is higher than 6×10^{-3}, which is over the apparatus operational limit of pressure. On the other hand, compositions lower than 2×10^{-3} were difficult to visualize. Therefore, the composition range between 3×10^{-3} and 6×10^{-3} was chosen. Binary system CO_2 (1) + coumarin (2) data are given in Figure 3 with pressure error bars.

The extractive method applied by Rodrigues et al. (2008) resulted in higher values of solubility, which may have occurred owing to the fact that it was in a supersaturation zone. This effect can be avoided using the static synthetic method. In addition, it is not possible to visualize both a homogeneous phase and phase transition through the extractive method.
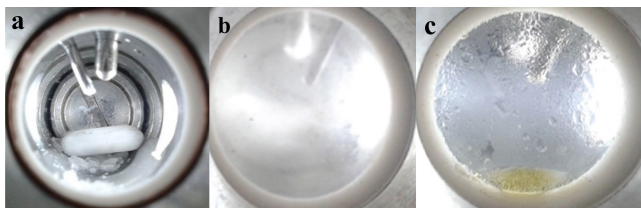

Figure 2. Equilibrium cell during experiments. a) Solid coumarin before pressurization. b) First moment of liquid coumarin precipitation. c) Coumarin accumulates as pressure decreases.
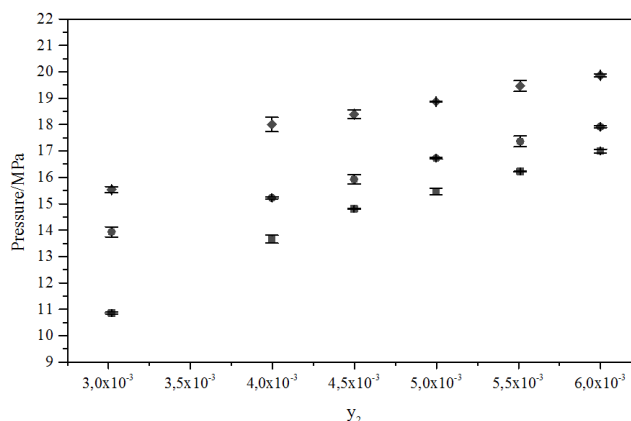
Figure 3. Pressure-composition diagram for the system CO_2 (1) + Coumarin (2); (■) 318 K, (●) 328 K, (◆) 338 K.

Yoo et al. (1997) determined solubility values of coumarin in supercritical CO_2 using a microscale apparatus through the analytical method. The authors observed lower values than those found in the present work. Despite the difference, solubility data obtained in this study were intermediate and similar to those reported in the literature. Figure 4 shows coumarin in supercritical CO_2 studied in past works using different methods.

Coumarin solubility increased with increasing phase transition pressure at a given temperature. Contrary to this study, both methods found in the literature describe a crossover temperature in solubility. This can be mainly related to the different methods used. Another point to observe is the temperature range. In this work the temperature range was 318-338 K, whilst for Rodrigues et al (2008) it was 308-328 K, and for Yoo et al. (1997) the temperature range was 308-323 K.
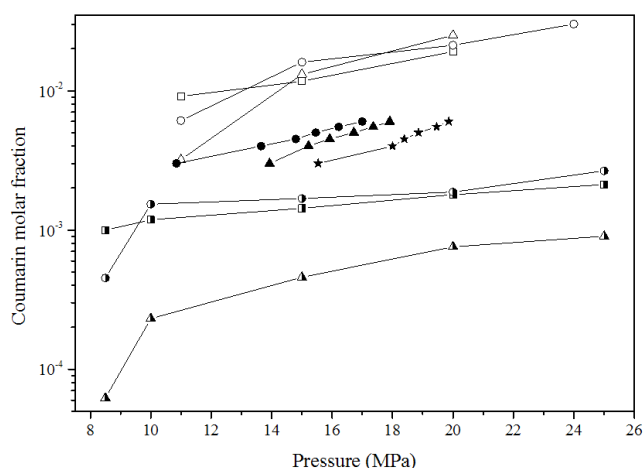
Figure 4. Solubility data for coumarin in supercritical CO_2 from this study at 318 K (●), 328 K (▲) and 338 K (★), from Rodrigues et al. (2008) at 308 K (□), 318 K (○) and 328 K (△), and from Yoo et al. (1997) at 308 K (■), 313 K (◑) and 323 K (▲).

In this study, the composition ranged between 3.0×10^{-3} and 6.0×10^{-3}. As for the other works, the composition range resulted in 0.91×10^{-2} - 3.01×10^{-2} (Rodrigues et al, 2008), and 1.0×10^{-3} - 2.66×10^{-3} (Yoo et al, 1997). Then, although crossover was not observed in experimental data in the present study, it could occur with different composition values that were not analysed.

Modeling Results

Table 2 presents the parameter values of k_{ij} and l_{ij} calculated for this study.

Figure 5 shows the correlation of all experimental data obtained using the PR-EoS. These data express the predicted values of solubility. The thermodynamic modeling used here can correlate the experimental data satisfactorily.

The model used in this work agrees with the experimental data. Absolute pressure average deviations (AAD%) were 4.6%, 1.6% and 2.5% for 318, 328 and 338 K isothermal, respectively.

Although there was no crossover in the experimental data, this phenomenon tended to occur at higher compositions, first with the isotherms 318 and 328 K, and then with isotherms 318 and 338 K, according to the calculated pressure transitions shown in Figure 5. The difference in pressure may be related to the distinct methodology and different

Table 2. Fitted parameters for each temperature using the experimental data obtained in this work.

T (K)	Parameters	
	k_{12}	l_{12}
318	0.1674	0.0045
328	0.1691	0.0026
338	0.1836	0.0126
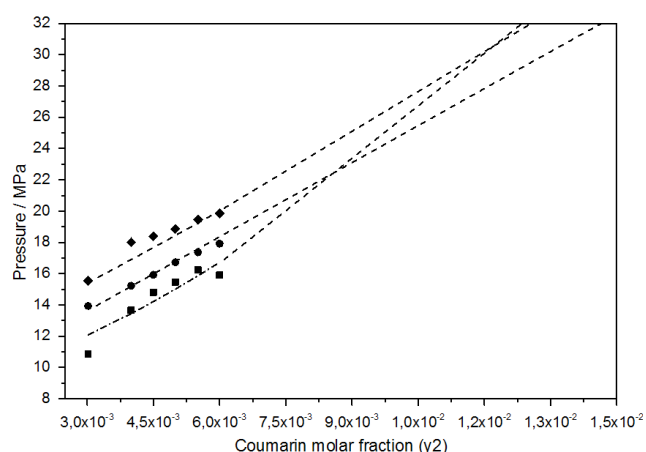
Figure 5. Experimental and calculated pressure transitions for the binary system CO₂ (1) + coumarin (2) at T = 318 K (■); 328 K (●); 338 K (◆). Calculations with the Peng-Robinson equation of state (----) and parameters from Table 2.

temperature, pressure and solubility used in other works available in the literature (Rodrigues et al, 2008; Yoo et al, 1997).

CONCLUSIONS

This phase equilibrium study reported new VLE equilibrium data for the binary system CO₂ (1) + coumarin (2). The analyzed system has characteristics of a type II transition. The static synthetic method was used with temperatures ranging from 318 K to 338 K. Maximum pressure obtained was close to 20 MPa. The Peng-Robinson equation of state calculated satisfactorily the phase equilibrium of CO₂ (1) + coumarin (2) system. Data reported in the present study are similar to experimental data found in the literature. Differences in concentrations as compared to the literature may be attributed to the experimental methodologies used. Moreover, the temperature range studied should also be observed.

The visual identification of the phase transition type for the measured system was not trivial due to the melting point depression phenomenon and the high asymmetry between the CO₂ molecule and coumarin. Near the phase transition point, the depressurization rate was decreased to avoid supersaturation. Although measured experimental data did not show crossover such as those in literature, it was possible to predict crossover using the PR-EoS with the binary parameters. These results show the robustness of the model applied and the experimental data consistency.

LIST OF SYMBOLS

y_2	Mole fraction of coumarin
ϕ_2^{∞}	Fugacity coefficient of coumarin at infinite dilution
a	van der Waals mixing rules parameter
b	van der Waals mixing rules parameter
k_{ij}	Binary interaction parameters
l_{ij}	Binary interaction parameters.
T_c	Critical temperature
P_c	Critical Pressure
ω	Acentric factor
PR-EoS	Peng-Robinson - Equation of State
P_{calc}	Calculated Pressure
P_{exp}	Experimental Pressure
AAD	Absolute average deviations

REFERENCES

Borges, F., Roleira, F., Milhazes, N., Santana, L., Uriarte, R. Simple coumarins and analogues in medicinal chemistry: occurrence, synthesis and biological activity, Curr Med Chem., 12, 887-916 (2005). https://doi.org/10.2174/0929867053507315

Castier, M. XSEOS: An Open Software for Chemical Engineering Thermodynamics, Chem. Eng. Educ., 2008, 42, 74-81 Spring (2008).

Dohrn, R., Peper, S., Fonseca, J.M.S. Fluid Phase Equilibria High-pressure fluid-phase equilibria: Experimental methods and systems investigated (2000-2004), Fluid Phase Equilibria, 288 1-54 (2010). https://doi.org/10.1016/j.fluid.2009.08.008

Ferreira-Pinto, L., Zanette, A., Augusto, F., Voll, P., Cabral, V.F., Castier, M., Rosana, C., Vapor - Liquid Equilibrium of Carbon Dioxide + Ethyl Acetate + Oleic Acid Mixtures at High Pressures, J. Chem. Eng. Data., 62, 2855-2860 (2017). https://doi.org/10.1021/acs.jced.7b00163

Ferreira, M.O., Ferreira-Pinto, L., Souza, E.M.B.D., Castier, M., Voll, F.A.P., Cabral, V.F., Cardozo-Filho, L. Experimental Vapor-Liquid Equilibria for the Systems {2-Ethyl-1-hexanol + Glycerol + CO_2} and {2-Methyl-2-propanol + Glycerol + CO_2}, J Chem Eng Data., 58, 2506-2512 (2013). https://doi.org/10.1021/je400398e

Fylaktakidou, K.C., Hadjipavlou-Litina, D.J., Litinas, K.E., Nicolaides D.N. Natural and synthetic coumarin derivatives with anti-inflammatory/ antioxidant activities, Curr Pharm Design., 10, 3813-3833 (2004). https://doi.org/10.2174/1381612043382710

Giufrida, W.M., Pinto, L.F.; Zanette, A.F., Voll, F.A.P., Kunita, M.H., Cabral, V.F., Cardozo-Filho, L. Liquid-vapor equilibrium data of CO_2 + dichloromethane + medroxyprogesterone system, Fluid Phase Equilibr., 362, 307-312 (2014). https://doi.org/10.1016/j.fluid.2013.10.037

Giufrida, W.M., Cabral, V.F., Cardoso-Filho, L., Conti, D. dos S., Campos, V.E.B. de, Rocha, S.R.P. da. Medroxyprogesterone-encapsulated Poly(3-hydroxybutirate-co-3-hydroxyvalerate) Nanoparticles using Supercritical Fluid Extraction of Emulsions, J. Supercrit. Fluids, 118, 79-88 (2016). https://doi.org/10.1016/j.supflu.2016.07.026

Hamdi, N., Puerta, M.C., Valerga, P. Synthesis, structure, antimicrobial and antioxidant investigations of dicoumarol and related compounds, Eur J Med Chem., 43, 2541-2548 (2008). https://doi.org/10.1016/j.ejmech.2008.03.038

Lanças, F.M., Assis, L.M., Souza, A.J., Kampen, M.H.V. Bassetto-Filho, A. Novas aplicações de sistemas SFE "home made". I. Plantas medicinais brasileiras, Food Sci Tech-Brazil, 17 (1997). https://doi.org/10.1590/S0101-20611997000400014

Lian, Z., Epstein, S.A., Blenk, C.W., Shine, A.D. Carbon dioxide-induced melting point depression of biodegradable semicrystalline polymers, J. Supercrit. Fluids., 39, 107-117 (2010). https://doi.org/10.1016/j.supflu.2006.02.001

Matos, M.J., Terán, C., Pérez-Castillo, Y. Uriart, L., Santana, E., Vina, D. Synthesis and study of a series of 3-arylcoumarins as potent and selective monoamine oxidase B inhibitors, J Med Chem., 54, 7127-7137 (2011). https://doi.org/10.1021/jm200716y

Matos, M.J., Mura, F., Vazquez-Rodriguez, S., Borges, F., Santana, L., Uriarte, E., Olea-Azar, C. Study of Coumarin-Resveratrol Hybrids as Potent Antioxidant Compounds, Molecules., 20, 3290-3308 (2015). https://doi.org/10.3390/molecules20023290

McHugh, M., Krukonis, V. Supercritical Fluid Extraction; Butterworth-Heinemann. Stoneham, (1994).

Oliveira, A.L., Pozza, L.N.L., Kamimura, E.S., Vicente, E., Cabral, F.A. Supercritical extraction of coumarin from guaco (Mikania laevigata and Mikania glomerata) for pharmaceutical applications, J Supercrit Fluid., 83, 65-71 (2013). https://doi.org/10.1016/j.supflu.2013.07.019

Panteleon, V., Kostakis, I.K., Marakos, P., Pouli, N., Andreadou, I. Synthesis and free radical scavenging activity of some new spiropyranocoumarins, Bioorg Med Chem Lett., 18, 5781-5784 (2008). https://doi.org/10.1016/j.bmcl.2008.09.065

Pinto, L.F., Rodriguez-Reartes, S.B., Corazza, M.L., Cabral, V.F., Araújo, P.H.H., Madureira, E.H., Zabolay, M.S., Cardozo-Filho, L. Phase behavior of carbon dioxide+medroxyprogesterone acetate system at high pressures, Fluid Phase Equilibr., 349, 1-11 (2013). https://doi.org/10.1016/j.fluid.2013.03.019

Poling, B.E., Prausnitz, J.M., O'Connell, J.P. The Properties of Gases and Liquids, fifth ed., McGraw-Hill, New York, (2000).

Reverchon, E., De Marco, I. Supercritical fluid extraction and fractionation of natural matter, J. Supercrit. Fluids., 38, 146-166 (2006). https://doi.org/10.1016/j.supflu.2006.03.020

Rodrigues, R.F., Tashima, A.K., Pereira, R.M.S., Mohamed, R.S. Cabral, F.A. Coumarin solubility and extraction from emburana (Torresea cearensis) seeds with supercritical carbon dioxide, J Supercrit Fluid., 43, 375-382 (2008). https://doi.org/10.1016/j.supflu.2007.07.014

Symeonidis, T., Chamilos, M., Hadjipavlou-Litina, D.J., Kallitsakis, M., Litinas, K.E. Synthesis of hydroxycoumarins and hydroxybenzo[f]- or [h] coumarins as lipid peroxidation inhibitors, Bioorg Med Chem Lett., 19, 1139-1142 (2009). https://doi.org/10.1016/j.bmcl.2008.12.098

Tabart, J., Kevers, C., Pincemail, J., Defraigne, J.O., Dommes, J. Comparative antioxidant capacities of phenolic compounds measured by various tests, Food Chem., 113, 1226-1233 (2009). https://doi.org/10.1016/j.foodchem.2008.08.013

Vilegas, J.H.Y., Marchi, E., Lanças, F.M. Extraction of Low-Polarity Compounds (with Emphasis on Coumarin and Kaurenoic Acid) from Mikania glomerata (Guaco) Leaves., Phytochem Analysis, 8, 266-270 (1997). https://doi.org/10.1002/(SICI)1099-1565(199709/10)8:5%3C266::AID-PCA363%3E3.0.CO;2-Q

Yoo, K.-P., Shin, H.Y., Noh, M.J., You, S.S. Measurement and modeling solubility of bioactive coumarin and its derivatives in supercritical carbon dioxide, Korean J. Chem. Eng., 14, 341-346 (1997). https://doi.org/10.1007/BF02707049

Zanette, A.F., Ferreira-Pinto, L., Giufrida, W.M., Zuber, A., Feirhmann, A.C., Castier, M., Cardozo-Filho, L., Cabral, V.F. Vapor-Liquid Equilibrium Data for Carbon Dioxide + (R , S)-1,2-Isopropylidene Glycerol (Solketal) + Oleic Acid Systems at High Pressure, J Chem Eng Data., 59, 1494-1498 (2014). https://doi.org/10.1021/je401051d