

Prediction of the Solubility of Aromatic Compounds from Brazilian Roasted Coffee (2-Methylpyrazine; 2-Furfuryl alcohol; 2,5-Dimethylpyrazine; γ -Butyrolactone and 2-Furfurylacetate) in SC-CO₂

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The solubility data for a mixture of five compounds present in the aromatic fraction of Brazilian roasted coffee (2-methylpyrazine, 2-furfuryl alcohol, 2,5-dimethylpyrazine, γ -butyrolactone and 2-furfurylacetate) in supercritical carbon dioxide (SC-CO₂) were determined at pressures from 250 to 300 bar and temperatures from 40 to 70°C. The solubilities of each of these five pure compounds in SC-CO₂ were also determined at 250 bar at the same temperatures. These compounds represent important classes of the coffee aroma (pyrazines, furans and lactones) and the data presented in this work is valuable to assess the solubility behavior of the aromatic fraction of roasted coffee oil in SC-CO₂. Data modeling was carried out using the Peng-Robinson equation of state with the classical mixing rule proposed by van der Waals (PR) and the empirical composition mixing rule of Stryjek–Vera (PR–SV) to describe the behaviour of the supercritical fluid phase. These models were used to determine the binary interaction parameters for 2-methylpyrazine(2)–SC-CO₂(1), 2-furfuryl alcohol(3)–SC-CO₂(1), 2,5-dimethylpyrazine(4)–SC-CO₂(1), γ -butyrolactone(5)–SC-CO₂(1) and 2-furfurylacetate(6)–SC-CO₂(1). Maximum solubility was observed for these compounds between 45 and 60°C at both pressures. The experimental solubility data were predicted by the PR and PR–SV models for the binary mixtures but not for the mixture of all five compounds. Experimental data presented in this work contributes to a better understanding of the extractability of roasted coffee oil using SC-CO₂.

Introduction

Supercritical fluid extraction requires the dissolution and transportation of the soluble compounds and the development of this technology may aid in the determination of the properties of several mixtures. The solubility of a solute in supercritical fluids is the most important property because it provides the solute concentration, which can be used as a basis for determining the approximate conditions for the extraction process. The application of supercritical fluid extraction in food/ingredient processing has gained popularity in recent years due to its ability to selectively extract desirable compounds without the presence of any contaminat-

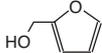
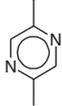
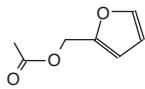
ing solvent or other undesirable compounds. SC-CO₂ is often used in supercritical extraction due to the fact that it is non-flammable, odourless, chemically inert and easily disposed of at relatively low cost. The low critical temperature (31.1°C) permits the extraction of thermally sensitive compounds.

SC-CO₂ extraction has been studied in relation to its commercial application for the extraction of roasted coffee oil with aromatic constituents (Roselius *et al.*, 1982; Nichtnennung, 1995; Ramos *et al.*, 1998; Oliveira *et al.*, 2001). Roasted coffee oil is constituted of lipids and many classes of aromatic compounds (Khan and Brow, 1953; Frield *et al.*, 1971; Wang *et al.*, 1983; Liardon and Ott, 1984; Dart and Nursten, 1985; Silmar and Lüllmann, 1993; Semmelroch and Grosh, 1995, 1996). It is a product of high market value for the confectionery, beverage, alcoholic beverage, bakery and even instant coffee, but the solubility data of these aromatic compounds in SC-CO₂ are still unknown. To obtain a roasted coffee oil rich in aromatic

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Table 1 Pure compounds (Aldrich Chemical Co. Inc.)

Compound	Structure	Density [g mL ⁻¹]	Purity [%]	<i>M</i> [g mol ⁻¹]
2-Methylpyrazine		1.030	99	94.12
2-Furfuryl alcohol		1.135	99	98.10
2,5-Dimethylpyrazine		0.990	98	108.14
γ -Butyrolactone		1.120	99	86.09
2-Furfuryl acetate		1.135	99	98.10

fraction, the solubilities of the aromatic compounds need to be known. The five aromatic compounds present in higher concentrations in the roasted coffee oil obtained by SC-CO₂ extraction, 2-methylpyrazine; 2-furfuryl alcohol; 2,5-dimethylpyrazine; γ -butyrolactone and 2-furfuryl acetate, were chosen to represent the solubility behaviour of the aromatic fraction of roasted coffee in SC-CO₂. Pyrazines are volatile heterocyclic compounds with nitrogen in their structure, which are abundant in coffee aroma and important in the aromatic composition of other foods. They are mainly formed in reactions that involve sugar and amino acids at high temperatures (Leahy and Reineccius, 1989; Bemis-Young *et al.*, 1993; Hwang *et al.*, 1993; Jusino *et al.*, 1997; D'Agostino *et al.*, 1998; Shu, 1999). Pyrazines are present in roasted coffee and in other roasted seeds: cocoa, sesame, peanut and soy beans (Wang *et al.*, 1983; Hashim and Chaveron, 1995; Semmelroch and Grosh, 1995; Shimoda *et al.*, 1996; Sanagi *et al.*, 1997; Buttery *et al.*, 1999; Jung *et al.*, 1999). Furans are compounds present in roasted coffee in a wide range of structures and, as a consequence, the aroma qualities they impart are also varied. Many furans are produced by the pyrolysis of sugar, with an aroma similar to that of caramel. 2-Furfuryl alcohol is important in roasted coffee aroma because it contributes to the burnt smell and bitter taste of the beverage. 2-Furfuryl alcohol and 2-furfuryl acetate are present in roasted coffee aromatic oil (Liardon and Ott, 1984; Roberts and Bertsch, 1987; Ramos *et al.*, 1998; Maeztu *et al.*, 2001) and were chosen to represent the furan compounds in the aromatic fraction of the roasted coffee oil. Solubility data for these five compounds in SC-CO₂ were determined for Brazilian coffee beans as well as the solubility data of the pure compounds. The experimental results for the

five pure compounds were correlated according to the Peng Robinson (Peng and Robinson, 1976) equation of state (PR) using two different mixing rules, the classical one of van der Waals and the composition-dependent one of Stryjek-Vera (Stryjek and Vera, 1986).

1. Experimental

1.1 Materials

Brazilian coffee beans (*Coffea arabica*) were roasted at 238°C for 10 min (coffee kindly donated by COCAM). The beans were ground according to the granulometry normally used in the soluble solids extraction. The granulometry was maintained the same since little modification occurred during the SC-CO₂ extraction, so the beans could still be used for the soluble solids extraction process without damaging the filters.

The pure compounds were purchased from Sigma-Aldrich Co. The chemical structure and some properties of the compounds are presented in **Table 1**. High-purity CO₂ (more than 99%) was supplied by White Martins Praxair Inc. Ethyl acetate, CAS: 141-78-6, with 99.8% of purity (EM SCIENCE) was used.

1.2 Equipment

The solubilities of 2-methylpyrazine; 2-furfuryl alcohol; 2,5-dimethylpyrazine; γ -butyrolactone and 2-furfuryl acetate in SC-CO₂ were experimentally determined using a static system method. The equipment employed is schematically shown in **Figure 1**. The ground roasted coffee beans were packed into a preheating equilibrium cell (6). The liquefied carbon dioxide from the gas cylinder (1) was passed through a cooling unit (2 and 3) to prevent vaporisation of CO₂ due to warming up and directed by a positive-displacement liquid

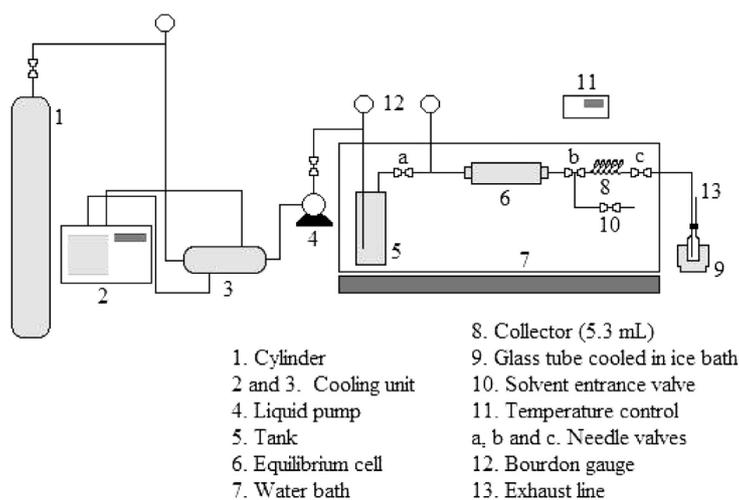


Fig. 1 Experimental equipment (static system)

pump (4) (AA-100-S, Eldex Laboratories, Inc.) into a preheating tank (5). The pressurised solvent was preheated up to extraction temperature before entering the equilibrium cell (6). At this time all the valves were closed. In the first step, valve (a) was opened and the equilibrium cell (6) loaded with CO₂ up to the desired pressure and thermostatically controlled at a given temperature. Valve (a) was then closed. The ground roasted coffee beans and the SC-CO₂ were maintained in contact for 10 h (static period). This cell was constructed from 316 stainless steel with a volume of 66 cm³. The equilibrium pressure was monitored by calibrated Bourdon gauges (12) (accuracy $\pm 0.5\%$) and the desired temperature controlled by immersion in a water bath (7) with a temperature control accuracy of $\pm 1^\circ\text{C}$. The equilibrium was reached after 10 h, since in the studies using three different times, 5, 10 and 15 h it was observed that the volatile concentration was lower when 5 h was used as equilibrium time, but that the same values were obtained after 10 and 15 h.

The SC-CO₂ saturated with the compounds after 10 h in equilibrium, passed through a transfer line including a collector (8) with a volume of 5.3 mL. The pressure in the system during the trapping of the SC-CO₂ saturated with the compounds was maintained constant. After the static period, the pump (4) was activated to pressurise the tank (5) at 50 bar above that of the equilibrium cell (6) and the needle valves (a and b) were then opened simultaneously such that the SC-CO₂ saturated with the compounds was displaced to the collector (8). The SC-CO₂ saturated with the compounds and displaced to the collector (8) was decompressed through an expansion valve (c) and introduced into a glass tube cooled in an ice bath (9). Gaseous CO₂ was exhausted and the compounds separated in the tube. Ethyl acetate was introduced into the system to rinse the collector (8) and pumped through the valve (10) in

order to obtain the solutes quantitatively in 2 mL of solution in the glass tube (9). Ethyl acetate was used as the solvent since it diluted the aromatic compounds present in the roasted coffee better than other solvent with different polarity as acetone, dichloromethane and hexane (Oliveira *et al.*, 2001). The solutes present in the sample were analysed off-line by gas chromatography and mass spectrometry (GC-MS).

1.3 Experimental design

In the first experiment, the solubilities of a mixture of five compounds (2-methylpyrazine; 2-furfuryl alcohol; 2,5-dimethylpyrazine; γ -butyrolactone and 2-furfuryl acetate) in SC-CO₂ obtained from roasted coffee beans, were determined.

In the second experiment, the solubility of each pure compound in SC-CO₂ was determined. A model in which the pure compounds (2 mL) were individually fixed in inert roasted coffee beans (25.22 ± 2.89 g) was assumed. The inert beans were prepared by a preliminary treatment in which the oil of the roasted coffee beans was extracted in a Soxhlet extractor using petroleum ether for 16 h. These oil free beans were subjected to extraction of the soluble solids with hot water (80°C) until clear water was obtained, and then dried at 105°C to constant weight. The pure compounds were fixed in these inert roasted coffee beans by spraying and immediately packed in the equilibrium cell. Inert roasted coffee beans were used, aiming at simulating the real situation. The pores formed during roasting permits penetration of the compound, instead of just remaining on the surface as occurs when glass beads are used. In the inert beans, there was no influence from the other compounds.

The solubilities of the roasted coffee compounds in SC-CO₂ were measured at 250, 275 and 300 bar and temperatures from 40 to 70°C. The selection conditions were in accordance with the preliminary

optimisation (Oliveira *et al.*, 2001). For the pure compounds, the solubilities were measured at 250 bar in the same temperature range.

1.4 GC-MS

The GC-MS apparatus was a gas chromatograph (HP 5890 series III, Hewlett Packard Co.) and a mass spectrometer (HP 5988A, Hewlett Packard Co.) equipped with a split/splitless injector (maintained at 200°C) and a capillary column HP Ultra 2 (25 m, 0.2 mm, 0.33 µm, Hewlett Packard Co.). Helium was used as the carrier gas with an inlet pressure of 15 psi. The split ratio was 1:50 and the volume of each injected sample was 1.0 µL. For the analysis of the coffee extract the GC oven was programmed to operate from 50 to 300°C (from 50 to 60°C at 1°C min⁻¹; from 60 to 200°C at 10°C min⁻¹; from 200 to 300 °C at 5°C min⁻¹). For the pure compounds, the GC oven temperature was programmed from 50 to 140°C (from 50 to 60°C at 1°C min⁻¹; from 60 to 140°C at 5°C min⁻¹). The ion source temperature was 250°C. Data acquisition was performed for the mass range from 50 to 500 *m/z*. The ionisation energy of electrons was 70 eV. The preliminary identification of the compounds was based on a comparison of experimentally obtained mass spectra with the NIST and Wiley 275-L mass spectra libraries (John Wiley & Sons, Inc.). By using the same temperature program, the concentration of these solutes was computed from the peak areas using the calibration method of the external standard, which was a solution of known concentration of the five pure compounds.

1.5 Solubility measurement

The solubility of the five compounds in SC-CO₂ was determined from the following Eq. (1) as a function of the mass of the solute, volume of the collector (8) and the density of the carbon dioxide (ρ) at each pressure and temperature studied.

$$S = \frac{x}{V \cdot \rho_{\text{CO}_2}} \quad (1)$$

where S is the solubility [g-solute/g-CO₂], x the mass of the solute [g-solute], V is the volume of the collector (8) (5.3 mL) and ρ the density of SC-CO₂ [g-CO₂/mL].

1.6 Thermodynamic modelling

The experimental results of the solubilities of the five compounds in SC-CO₂ were correlated using a solution method. Modelling the solubility of substances in SC-CO₂ is important in SCF-process designing. The most rigorous methods consist of calculating the fugacity of the solute in the SCF-phase assuming that it behaves as a dense gas or as an expanded liquid. Standard thermodynamic relationships made by equating fugacities in the condensed (L) and SCF-phases for each compound (Eq. (2)), could be used to calculate the L-SCF equilibrium:

$$f_i^L = f_i^{\text{SCF}} \quad (2)$$

The fugacities can be expressed by the following equation:

$$\left(\phi_i^L p x_i = \phi_i^{\text{SCF}} p y_i\right)_T \quad (3)$$

where p is the equilibrium pressure and x_i and y_i are the molar fractions of component i in the condensed and SCF-phases, respectively. The fugacity coefficient ϕ_i was evaluated using the Peng–Robinson equation of state (Peng and Robinson, 1976):

$$p = \frac{RT}{V-b} - \frac{a}{V(V+b) + b(V-b)} \quad (4)$$

and also the conventional mixing rule of van der Waals (Eq. (5)) and the dependent composition rule of Stryjek–Vera (Stryjek and Vera, 1986) (Eq. (6)), where Ka_{ij} and Ka_{ji} are the binary interaction parameters between the unlike molecules i and j .

$$a_m = \sum_i \sum_j x_i x_j (1 - Ka_{ij}) (a_{ii} a_{jj})^{1/2} \quad (5)$$

$$a_m = \sum_i \sum_j x_i x_j (1 - x_i Ka_{ij} - x_j Ka_{ji}) (a_{ii} a_{jj})^{1/2} \quad (6)$$

The calculation of the phase equilibrium composition using the PR and PR–SV equations of state is possible by using the properties of the pure compounds listed in **Table 2**, which were estimated by the group contribution methods (Joback and Reid, 1987; Somayajulu, 1989) and the acentric factor, according to the following relation:

$$\omega = \frac{3}{7} \left(\frac{T_b}{T_b - T_c} \right) \log_{10} \left(\frac{p_b}{p_c} \right) - 1.0 \quad (7)$$

The binary interaction parameters Ka_{ij} and Ka_{ji} for both mixing rules (**Table 3**) were treated as a fitting parameter using the binary data (**Table 4**). The parameter estimation was performed by minimising the following objective function, OF :

$$OF = \sum_{j=1}^N \sum_{i=1}^2 \left[\left(\frac{y_i^c - y_i^e}{y_i^e} \right)^2 \right]_j \quad (8)$$

where c and e denote the calculated and experimental values, respectively.

Table 2 Critical properties and acentric factors of the compounds

Compounds	ω	T_b [K]		T_c [K]			p_c		
		e	A	e	A	B	e	A	B
CO ₂ (1)	0.2250	—	—	304.10	—	—	73.75	—	—
2-Methylpyrazine(2)	0.3522	408.20*	448.08	—	631.25	603.21	—	53.67	47.51
2-Furfuryl alcohol (3)	0.7423	443.20*	456.38	—	632.55	632.47	—	55.28	49.63
2,5-Dimethylpyrazine(4)	0.3958	428.20 [#]	475.34	—	645.94	620.11	—	45.90	40.52
γ -Butyrolactone(5)	0.3777	477.70*	378.93	731.00 ^a	740.43	708.17	51.31 ^a	53.82	44.30
2-Furfurylacetate (6)	0.5718	450.20 [#]	506.25	—	645.83	640.56	—	39.76	34.65

A: Joback and Reid (1987), B: Somayajulu (1989), *Aldrich Chemical Co. Inc.

[#]Weast and Grasselli (1989), ^aWilson *et al.* (1996), K = Kelvin degree

Table 3 Binary interaction parameters fitted by use of experimental data at 250 bar

Systems	PR	PR–SV		Temperature [°C]
	$Ka_{ij} = Ka_{ji}$	Ka_{ij}	Ka_{ji}	
2-Methylpyrazine(2) SC-CO ₂ (1)	0.2530391	0.2149402	−0.0419656	40–70
2-Furfuryl alcohol(3) SC-CO ₂ (1)	0.1279375	0.1131269	0.0313026	40–70
2,5-Dimethylpyrazine(4) SC-CO ₂ (1)	0.2217188	0.1862343	−0.0216799	40–70
γ -Butyrolactone(5) SC-CO ₂ (1)	0.1106432	0.1251078	0.2531056	40–70
2-Furfurylacetate(6) SC-CO ₂ (1)	0.1806770	0.1939286	0.4641417	40–70

2. Results and Discussion

Figure 2 shows the total ion chromatogram for the SC-CO₂ soluble compounds present in roasted coffee, extracted using the static method. The aromatic compounds in higher concentrations (peaks 1, 2, 3, 4 and 5) were chosen to represent the solubility behaviour of the aromatic fraction of the roasted coffee in SC-CO₂.

Table 4 presents the experimental solubilities of the five pure compounds in SC-CO₂ at 250 bar and temperatures from 40 to 70°C. Under the same conditions of pressure and temperature, the solubilities of 2-methylpyrazine and 2-furfuryl alcohol were lower than those of the other three solutes. This may be due to the higher polarity of these compounds when dissolved in a non-polar solvent such as CO₂.

Table 5 presents the solubilities of these same five compounds from roasted coffee in SC-CO₂ at 250, 275 and 300 bar and temperatures from 40 to 70°C. The solubilities, experimentally determined in SC-CO₂, of the pure compounds (Table 4), were higher than those of the same compounds obtained from the roasted coffee (Table 5). This could be due to the presence of other

compounds, such as triacylglycerols, fatty acids, caffeine and other non-identified compounds soluble in SC-CO₂. Many soluble compounds all together, such as 2-methylpyrazine; 2-furfuryl alcohol; 2,5-dimethylpyrazine; γ -butyrolactone and 2-furfuryl acetate, will compete for the solvency capacity of the same quantity of SC-CO₂ in the extractor, at the same pressure and temperature. This changes the saturation concentration of the solvent. When the solubility of the pure compounds was measured, no interaction between the SC-CO₂ and other compounds present in the matrix (coffee beans) occurred.

Although the solubility of each pure compound in SC-CO₂ was higher than that of the same compound in the roasted coffee, in both cases the behaviour of the solubility of 2-methylpyrazine at 250 bar was the same (**Figure 3**), being maximum at 55°C. The same behaviour could also be observed for 2-furfuryl acetate (**Figure 4**), maximum solubility being observed at 60°C. The solubilities of the five compounds either pure or extracted from roasted coffee, showed their highest values at a determined temperature, but it did not coincide for all the compounds, only for 2-methylpyrazine and 2-furfuryl acetate.

Table 4 Experimental and calculated data of solubility of the five pure compounds in SC-CO₂ at 250 bar [g-solute/g-CO₂]

2-Methylpyrazine(2)					
T [°C]	S ₂ ^e	PR		PR-SV	
		S ₂ ^c	ΔS [%]	S ₂ ^c	ΔS [%]
40	2.30 × 10 ⁻²	2.00 × 10 ⁻²	13.05	2.01 × 10 ⁻²	12.96
50	2.66 × 10 ⁻²	2.50 × 10 ⁻²	6.13	2.42 × 10 ⁻²	9.23
55	2.95 × 10 ⁻²	2.77 × 10 ⁻²	6.17	2.63 × 10 ⁻²	10.72
60	2.70 × 10 ⁻²	3.05 × 10 ⁻²	12.84	2.85 × 10 ⁻²	5.74
70	2.69 × 10 ⁻²	3.63 × 10 ⁻²	35.22	3.31 × 10 ⁻²	23.20
Deviation [%]			14.68	12.37	
2-Furfuryl alcohol(3)					
T [°C]	S ₃ ^e	PR		PR-SV	
		S ₃ ^c	ΔS [%]	S ₃ ^c	ΔS [%]
40	2.73 × 10 ⁻²	2.78 × 10 ⁻²	1.86	2.85 × 10 ⁻²	4.41
50	3.20 × 10 ⁻²	3.09 × 10 ⁻²	3.52	3.11 × 10 ⁻²	2.87
55	3.29 × 10 ⁻²	3.23 × 10 ⁻²	1.97	3.22 × 10 ⁻²	2.14
60	3.56 × 10 ⁻²	3.37 × 10 ⁻²	5.44	3.33 × 10 ⁻²	6.36
70	3.33 × 10 ⁻²	3.63 × 10 ⁻²	8.92	3.54 × 10 ⁻²	6.29
Deviation [%]			4.34	4.42	
2,5-Dimethylpyrazine(4)					
T [°C]	S ₄ ^e	PR		PR-SV	
		S ₄ ^c	ΔS [%]	S ₄ ^c	ΔS [%]
40	3.74 × 10 ⁻²	2.23 × 10 ⁻²	40.24	2.67 × 10 ⁻²	28.72
50	4.59 × 10 ⁻²	2.75 × 10 ⁻²	39.99	3.13 × 10 ⁻²	31.74
55	3.91 × 10 ⁻²	3.02 × 10 ⁻²	22.76	3.36 × 10 ⁻²	14.09
60	3.79 × 10 ⁻²	3.30 × 10 ⁻²	12.85	3.59 × 10 ⁻²	5.14
70	2.82 × 10 ⁻²	3.86 × 10 ⁻²	37.10	4.04 × 10 ⁻²	43.35
Deviation [%]			30.59	24.61	
γ-Butyrolactone(5)					
T [°C]	S ₅ ^e	PR		PR-SV	
		S ₅ ^c	ΔS [%]	S ₅ ^c	ΔS [%]
40	3.85 × 10 ⁻²	4.24 × 10 ⁻²	9.91	4.08 × 10 ⁻²	5.77
50	4.15 × 10 ⁻²	4.24 × 10 ⁻²	2.20	4.22 × 10 ⁻²	1.57
55	4.96 × 10 ⁻²	4.21 × 10 ⁻²	15.07	4.25 × 10 ⁻²	14.30
60	4.32 × 10 ⁻²	4.16 × 10 ⁻²	3.74	4.26 × 10 ⁻²	1.47
70	3.96 × 10 ⁻²	4.01 × 10 ⁻²	1.27	4.21 × 10 ⁻²	6.34
Deviation [%]			6.44	5.89	
2-Furfurylacetate(6)					
T [°C]	S ₆ ^e	PR		PR-SV	
		S ₆ ^c	ΔS [%]	S ₆ ^c	ΔS [%]
40	2.92 × 10 ⁻²	3.51 × 10 ⁻²	20.26	3.38 × 10 ⁻²	15.94
50	4.47 × 10 ⁻²	4.13 × 10 ⁻²	7.62	4.10 × 10 ⁻²	8.16
55	4.90 × 10 ⁻²	4.43 × 10 ⁻²	9.67	4.47 × 10 ⁻²	8.82
60	5.53 × 10 ⁻²	4.72 × 10 ⁻²	14.68	4.84 × 10 ⁻²	12.55
70	5.26 × 10 ⁻²	5.28 × 10 ⁻²	0.30	5.57 × 10 ⁻²	5.96
Deviation [%]			10.51	10.29	

Deviation [%] = $\sum_i^N \left\{ \left[\frac{|S_i^e - S_i^c|}{S_i^e} \right] / N \right\} \times 100$, where N is the number of experimental data for each binary system, S_i^e is the experimental solubility data and S_i^c is the calculated solubility data

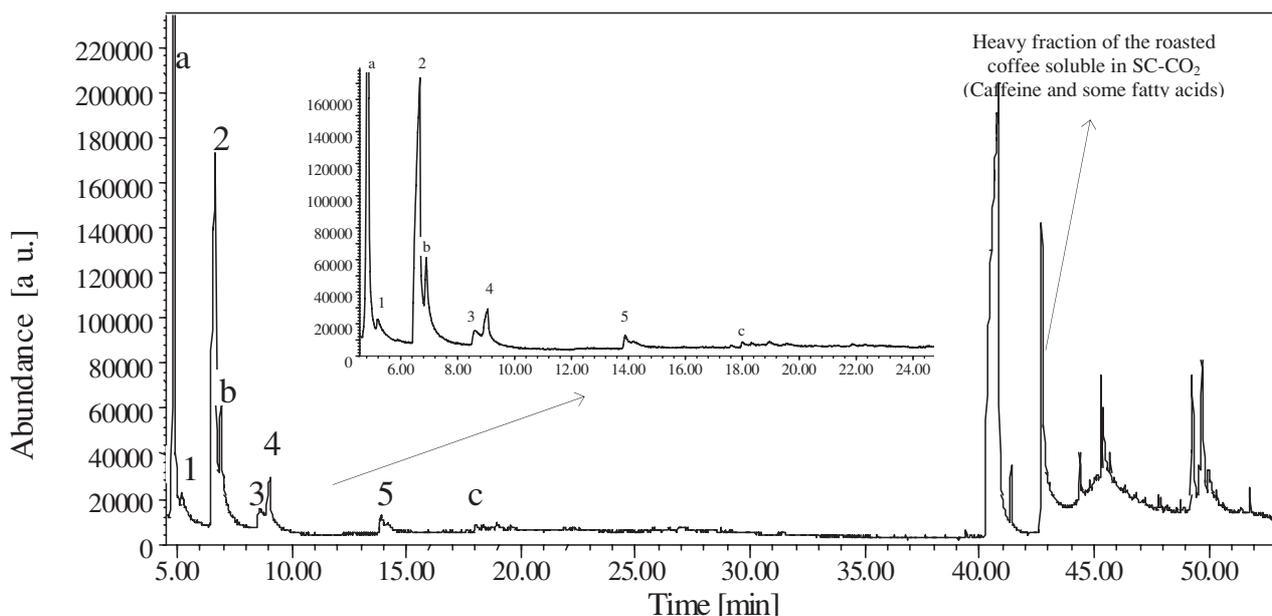


Fig. 2 Total ion chromatogram of the five SC-CO₂ soluble aromatic compounds from a roasted coffee oil sample (a. solvent; b. acetoxo propanone; c. guaiacol; 1. 2-Methylpyrazine; 2. 2-Furfuryl alcohol; 3. 2,5-Dimethylpyrazine; 4. γ -Butyrolactone; 5. 2-Furfurylacetate)

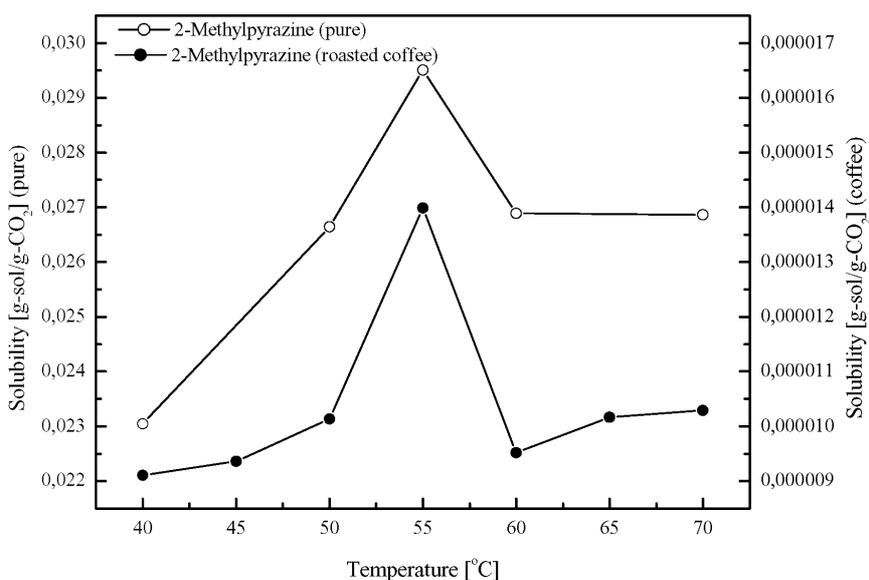


Fig. 3 Experimental solubility data for 2-methylpyrazine at 250 bar, pure and from roasted coffee

Comparing the solubility of the 2-methylpyrazine from roasted coffee in SC-CO₂ at different pressures (**Figure 5**), similar behaviour was observed at 250 and 300 bar, showing greater values at 55°C. However, when the three pressures were compared, the best solubility occurred at 50°C and 275 bar. Similar behaviour could be observed for γ -butyrolactone (**Figure 6**), in this case at 275 and 300 bar, where the greatest solubilities occurred at 50°C. At 250 bar the variation in solubility with temperature was different.

The average relative deviations (% deviation) between the calculated and experimental solubility data for the binary mixtures are presented in Table 4. The observed deviation was sufficiently small for the following binary systems: 2-furfuryl alcohol(3)-SC-CO₂(1); γ -butyrolactone(5)-SC-CO₂(1) and 2-furfurylacetate(6)-SC-CO₂(1). The results were practically the same for the two models evaluated PR and PR-SV. Only for the binary system γ -butyrolactone(5)-SC-CO₂(1) could the thermodynamic models predict the solubility behaviour,

Table 5 Solubility of the five compounds in roasted coffee aromatic oil in supercritical CO₂ [g-solute/g-CO₂]

<i>T</i> [°C]	250 [bar]	275 [bar]		300 [bar]	
	Solubility [g-solute/g-CO ₂]	Solubility [g-solute/g-CO ₂]	Deviation [%]	Solubility [g-solute/g-CO ₂]	Deviation [%]
2-Methylpyrazine					
40	9.10×10^{-6}	9.89×10^{-6}	—	9.61×10^{-6}	—
45	9.36×10^{-6}	7.84×10^{-6}	—	9.18×10^{-6} *	13.51
50	1.01×10^{-5}	2.52×10^{-5}	—	1.28×10^{-5}	—
55	1.40×10^{-5}	1.03×10^{-5} *	11.78	1.73×10^{-5}	—
60	9.52×10^{-6}	1.11×10^{-5}	—	1.18×10^{-5}	—
65	1.02×10^{-5}	1.41×10^{-5}	—	9.97×10^{-6}	—
70	1.03×10^{-5}	4.15×10^{-6}	—	—	—
2-Furfuryl alcohol					
40	1.25×10^{-4}	1.01×10^{-4}	—	1.43×10^{-4}	—
45	1.25×10^{-4}	1.28×10^{-4}	—	1.40×10^{-4} *	5.97
50	1.26×10^{-4}	2.90×10^{-4}	—	2.46×10^{-4}	—
55	1.31×10^{-4}	1.54×10^{-4} *	6.04	1.63×10^{-4}	—
60	1.54×10^{-4}	1.59×10^{-4}	—	1.91×10^{-4}	—
65	1.59×10^{-4}	1.45×10^{-4}	—	1.38×10^{-4}	—
70	1.06×10^{-4}	9.45×10^{-5}	—	1.36×10^{-4}	—
2,5-Dimethylpyrazine					
40	4.52×10^{-6}	3.94×10^{-6}	—	7.20×10^{-6}	—
45	6.01×10^{-6}	4.88×10^{-6}	—	7.24×10^{-6} *	15.59
50	5.86×10^{-6}	2.50×10^{-5}	—	1.41×10^{-5}	—
55	1.78×10^{-5}	7.46×10^{-6} *	13.01	1.75×10^{-5}	—
60	1.86×10^{-5}	1.76×10^{-5}	—	7.56×10^{-6}	—
65	8.06×10^{-6}	7.28×10^{-6}	—	7.14×10^{-6}	—
70	—	3.50×10^{-6}	—	7.20×10^{-6}	—
γ-Butyrolactone					
40	2.26×10^{-5}	3.49×10^{-5}	—	2.62×10^{-5}	—
45	3.60×10^{-5}	5.37×10^{-5}	—	5.56×10^{-5} *	2.29
50	3.65×10^{-5}	6.90×10^{-5}	—	6.66×10^{-5}	—
55	3.67×10^{-5}	6.50×10^{-5} *	3.89	4.86×10^{-5}	—
60	4.50×10^{-5}	3.83×10^{-5}	—	3.68×10^{-5}	—
65	3.87×10^{-5}	3.47×10^{-5}	—	3.63×10^{-5}	—
70	3.66×10^{-5}	3.45×10^{-5}	—	3.08×10^{-5}	—
2-Furfurylacetate					
40	1.42×10^{-5}	1.61×10^{-5}	—	1.62×10^{-5}	—
45	1.50×10^{-5}	3.51×10^{-5}	—	1.52×10^{-5} *	0.35
50	1.79×10^{-5}	3.57×10^{-5}	—	2.68×10^{-5}	—
55	2.73×10^{-5}	1.71×10^{-5} *	7.73	2.69×10^{-5}	—
60	3.36×10^{-5}	1.61×10^{-5}	—	1.61×10^{-5}	—
65	3.10×10^{-5}	1.64×10^{-5}	—	1.53×10^{-5}	—
70	2.92×10^{-5}	1.46×10^{-5}	—	1.56×10^{-5}	—

Deviation = $|\sigma|/\text{Average} \times 100$; *Arithmetic average of three measurements

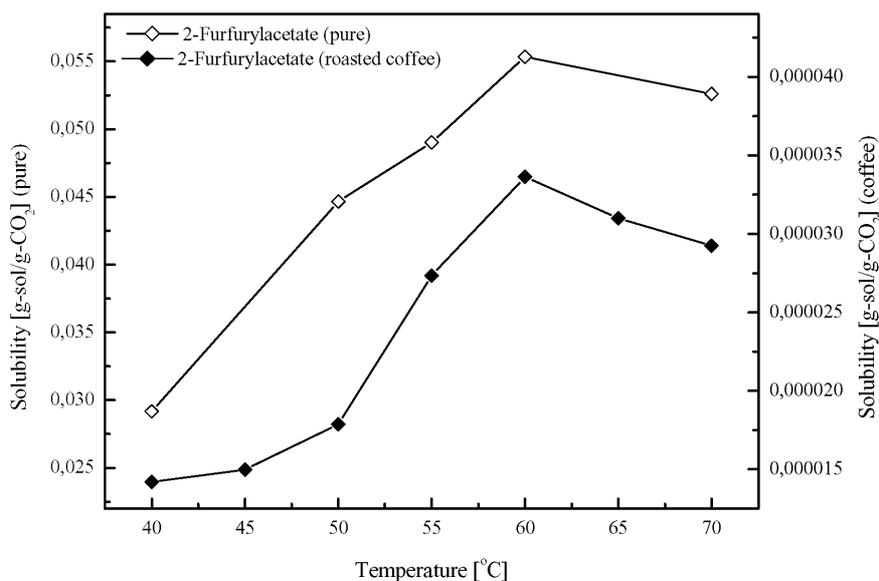


Fig. 4 Experimental solubility data for 2-furfurylacetate at 250 bar, pure and from roasted coffee

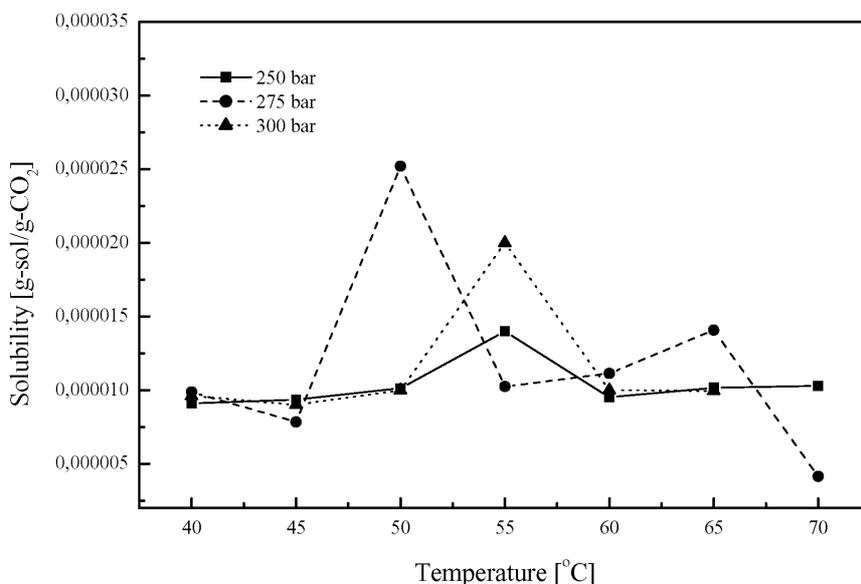


Fig. 5 Experimental solubility data for 2-methylpyrazine in supercritical CO₂ present in roasted coffee at different pressures

indicating a maximum value and describing an increase in solubility with increase in temperature followed by the reverse behaviour after reaching the maximum point (Figure 7).

Considering that the PR equation of state showed good fit for non polar compounds and that the systems analysed in this study were highly polar, it was possible to conclude that this model could present good correlation between calculated and experimental data for binary systems. However, high relative deviation was observed for some conditions such as the 2,5-dimethylpyrazine(4)–SC-CO₂(1) system at 40°C (Table 4).

The substitution of the classical mixing rule of van der Waals by dependent composition mixing rules has been used to extend the PR equation of state to the prediction of polar systems (Oliveira and Cabral, 1997; Velezmozo *et al.*, 2000; Raabe and Köhler, 2004). Nevertheless, this was not observed in this study. When a mixture of these five compounds was considered, the results obtained using the PR and PR–SV equations of state indicated that these models were unfit to predict the solubility behaviour of the aromatic mixture of the five compounds chosen to represent the aromatic fraction of roasted coffee.

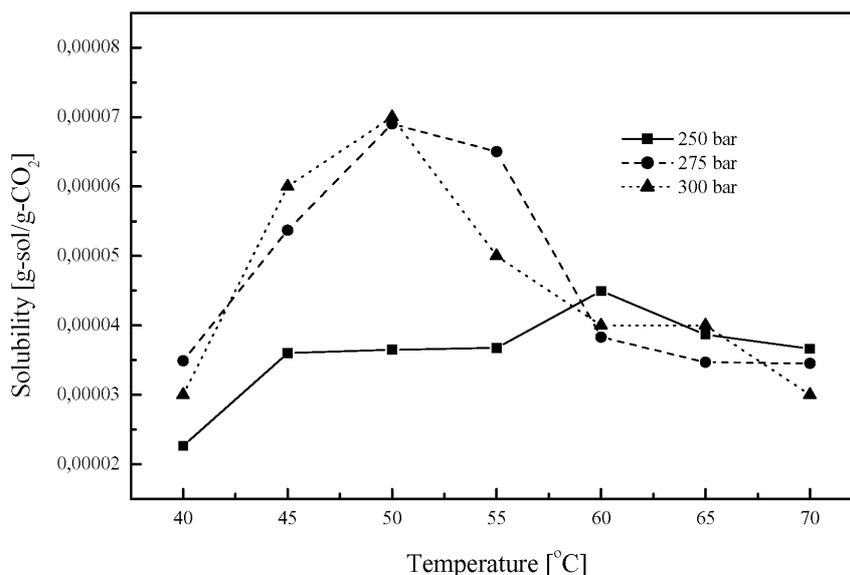


Fig. 6 Experimental solubility data of γ -butyrolactone in supercritical CO_2 , at different pressures from roasted coffee

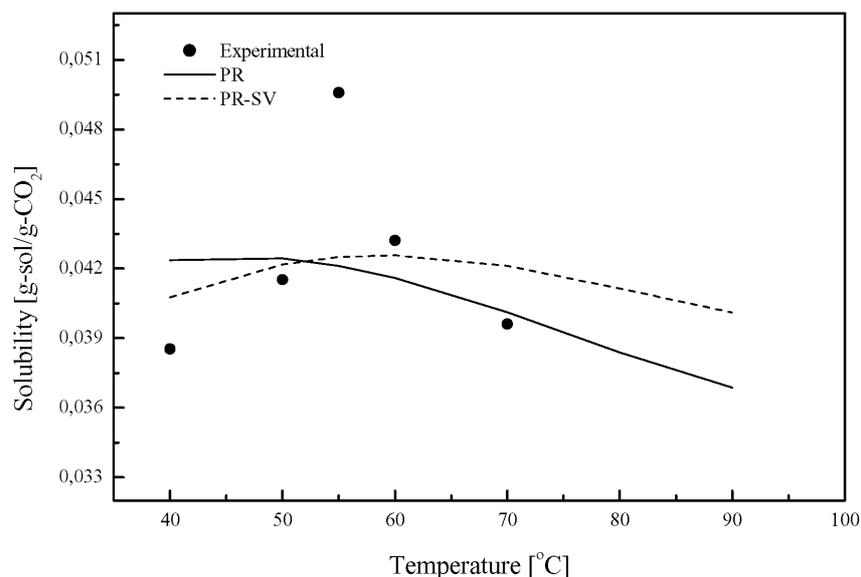


Fig. 7 Experimental and calculated data for the binary system: γ -butyrolactone(5)-SC- CO_2

Conclusions

The experimental data for the solubility of these five compounds in SC- CO_2 , pure or present in roasted coffee, indicate that the maximum values occurred at 275 bar and temperatures between 45 and 60°C. Under these conditions of pressure and temperature, the best yield in the roasted coffee aromatic oil when extracted by supercritical CO_2 was obtained by an experimental optimisation of the process carried out in a previous study (Oliveira *et al.*, 2001). The thermodynamic models that use the PR and PR-SV equations of state confirmed their capability of predicting the thermodynamic properties of a binary mixture, but could

not predict the solubility behaviour for the mixture of the five compounds.

However despite the fact that the PR equation of state is a conventional model widely used to predict phase equilibrium, its employment for mixtures such as those present in aromatic compounds from natural products is still restricted. We intend to carry out further studies employing the PR equation of state with different mixing rules, such as that proposed by Mathias *et al.* (1991), aiming to predict the phase equilibrium of similar high pressure systems, since this equation is simple and may be explored with thermodynamic models with applicability in this area.

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Nomenclature

a	= PR model parameter	[bar cm ⁶ g mol ⁻²]
a_m	= PR model parameter for mixture of compounds	[bar cm ⁶ g mol ⁻²]
b	= PR model parameter	[cm ³ g mol ⁻¹]
c	= calculated	
e	= experimental	
f	= fugacity	[bar]
GC-MS	= gas chromatography and mass spectrometry	
Ka_{ij}, Ka_{ji}	= binary interaction parameters between compounds i and j	
L	= liquid	
M	= molar mass	[g mol ⁻¹]
N	= number of experiments	
OF	= objective function	
PR	= Peng–Robinson equation of state	[bar]
PR–SV	= Peng–Robinson equation of state with the composition mixing rule of Stryjek–Vera	[bar]
p	= pressure	[bar]
p_b	= normal pressure	[bar]
p_c	= critical pressure	[bar]
S	= solubility	[g-solute/g-CO ₂]
SC-CO ₂	= supercritical carbon dioxide	
SCF	= supercritical fluid	
T	= temperature	[°C]
T_b	= normal boiling temperature	[K]
T_c	= critical Temperature	[K]
V	= volume	[mL, cm ³]
X	= concentration of the solute	[g-solute]
x_i	= mole fraction of component i in the condensed phase	
y_i	= mole fraction of component i in the SCF-phase	
ρ	= density	[g mL ⁻¹]
ϕ_i	= fugacity coefficient of component i	
ω	= acentric factor	

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