SOLUBILITIES OF 2-METHYLPYRAZINE; 2-FURFURYLALCOHOL; 2,5-DIMETHYLPYRAZINE; g-BUTYROLACTONE AND 2-FURFURYLACETATE IN SUPERCRITICAL CARBON DIOXIDE

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Five aromatic compounds, 2-methylpyrazine; 2-furfurylalcohol; 2,5-dimethylpyrazine; γ-butyrolactone and 2-furfurylacetate, were present in higher concentration in the roasted coffee aromatic oil obtained by supercritical extraction [1]. These compounds represent important classes of coffee aroma compounds (pyrazines, furans and lactones), and were chosen to perform the solubility behaviour of the aromatic fraction of roasted coffee in supercritical CO_2. The solubilities of these pure compounds were measured at 250 bar over temperature (T) range from 40 to 70 ^{o}C using a static system of extraction. The solubilities were determined from the mass of solute trapped by decompression and the volume of CO_2 in the collector after 10 h in equilibrium. The behaviour of the solubilities were observed for the pure compounds and for these compounds in roasted coffee aromatic oil, at pressure (P) of 250, 275 and 300 bar. A thermodynamic model that uses the equation of state of Peng-Robinson [2] with the classical missing rule of van de Waals, and the dependent composition mixing rule of Stryjek and Vera [3], it was used to predict the solubility behaviour of these compounds in supercritical CO_2 at different values of P and T.

INTRODUCTION

The principal coffee aromatic compounds are formed by the reactions that occurs during the roasting. The most important are the Maillard reaction, Strecker degradation, degradation of sugar, trigonelline, phenolic acids, lipids, proline, and hydroxyproline, and breakdown of sulphur and hydroxy amino acids [4]. Pyrazines are volatile compounds abundant in coffee aroma, and important in the aromatic composition of other foods. These are formed principally in reactions that involve sugar and amino acids at high T [5, 6, 7]. Pyrazines are present in roasted coffee, and in others roasted seeds: cocoa, sesame seed, peanut and soy beans [8, 9, 10, 11]. Furans are compounds present in roasted coffee in many different structures, and because of these, the aroma qualities that they impart are varied. Many furans are produced by the pyrolysis of sugar and have flavour similar to caramel aroma. The 2-furfurylalcohol is important in roasted coffee aroma because it collaborates to the burnt smell and bitter taste of the beverage. The 2-furfurylalcohol and 2-furfurylacetate are present in roasted coffee [12, 13, 14], and these were chosen to represent the furans in the roasted coffee aromatic oil. Five compounds were present in higher concentration in the roasted coffee aromatic oil obtained by supercritical extraction, and were chose to perform the behaviour of the solubility of the aromatic fraction of roasted coffee in supercritical CO_2. The Peng-Robinson equation of state has been used for calculation of phase equilibrium with applications in different areas. Recent studies have been carried out with the intention of improving the capacity of this equation to predict the solubility behavior of polar mixtures and other systems. Studies have been applied using different mixing rules trying to improve the fit of the binary interaction parameters. The objective of this work was fitting the

binary interaction parameters (Ka_{ij}) between the supercritical CO_2 and the main pure compounds presented in coffee oil using the Peng-Robinson equation of state [2]. To extend the use of the Peng-Robinson equation of state for mixture, it was used two mixing rules, those proposed by van der Waals and a composition dependant mixing rule of Stryjek & Vera [3].

MATERIALS AND METHODS

A static system that also could operated as a dynamic supercritical extractor [1] was used to measure the solubilities of 2-methilpyrazine; 2-furfurylalcohol; 2,5-dimethylpyrazine; γ-butyrolactone and 2-furfurylacetate in supercritical CO_2. The liquefied CO_2 leaving a gas cylinder was passed through a cooling unit, and directed to a positive-displacement liquid pump into a preheating equilibrium cell (extractor) containing roasted coffee grains. For the measurement of the solubility of pure compounds in supercritical CO_2, the grains of roasted coffee are preliminarily treated: the oil was extracted by Soxhlet extractor during 16 h. These oil free grains were subjected to a extraction of soluble solids with hot water ($80^{o}C$) and drying at $105^{o}C$ up to constant weight. The pure compounds were sprayed (2 mL) in the inert roasted coffee and immediately deposited in the equilibrium cell. Inert roasted coffee grains were used because of the pores formed during the roasted, which permits the penetration of the compounds, not retaining these only in the surface, promoting a similar real situation. The solubility of these five compounds in supercritical CO_2 was also measured in the roasted coffee aromatic oil obtained from Brazilian *Coffea arabica* in the same conditions and procedure. The supercritical CO_2 remained in equilibrium cell (66 cm^3) during a static time of 10 h. The equilibrium P was measured by Bourdon gauges (accuracy ± 0.3%), and the T was controlled by immersion in a thermal water bath with control accuracy of ± $1^{o}C$. The supercritical CO_2 saturated with the compounds after equilibrium was collected in a collector with known volume. To maintain the same P in the system during the collect, the pump was activated to pressurise a reservation tank 50 bar over the equilibrium cell, so two needle valves were open simultaneously, avoiding the drop in the P of the system: equilibrium cell – collector. The supercritical CO_2 saturated with the compounds displacement to the collector was decompressed through an expansion valve, and introduced into a glass tube cooled in ice bath. Gaseous CO_2 and the compounds were separated in the tube. The compound or the roasted coffee oil remnant in the collector was taken back with ethyl acetate through the solvent entrance valve, and collector resulting in 2mL of solution into the glass tube. The among of the sample trapped in the tube was determined by gas chromatography and mass spectrometry (GC/MS), (HP 5890 series III) with HP Ultra 2 (25m, 0.2mm, 0.33μm) capillary column. The concentration of these compounds was performed using the calibration method of the external standard. The conditions for analysis were: initial T of $50^{o}C$ whit a gradual increase of $1^{o}C$ per min. up to $60^{o}C$ during 1min., and a gradual increase of $5^{o}C$ per min. from $60^{o}C$ to the final T of $140^{o}C$. The injector and detector T were $200^{o}C$ and $250^{o}C$ respectively. The pure compounds were purchased from Sigma Aldrich Co. (Milwaukee, WI, USA). High-purity CO_2 (more than 99%) was supplied by White Martins Praxair Inc. Brazil. Ethyl acetate EM Science, CAS: 141-78-6, with 99.8% of purity was used. The solubility was determined according to equation (1), as a function of the mass of the compounds and volume of the collector.

$$S = \frac{x}{V.r_{CO_2}}$$ (1)

where: S, Solubility (g solute/g CO_2); x, Mass of solute (g solute); V, Volume of collector (15.9 mL), and r, Density of CO_2 (g CO_2/mL). The critical proprieties of this compounds were estimated by the methods of group contribution [15, 16]. **Table 1** shows the values of the critical properties (Tc and Pc), experimental or estimated, which has been adopted in the present work.

RESULTS

The measurement of the solubilities was carried out for several values of T (from 40 to 70°C) at P of 250 bar to the pure compounds (**Table 2**) and 250, 275 and 300 bar for the same compounds in the roasted coffee aromatic oil (**Table 3**). The solubilities of the pure compounds showed similar values in the same P and T.

It was also observed that the solubilities of the pure compounds (**Table 2**) was higher than the solubilities of these same compounds in the roasted coffee aromatic oil (**Table 3**). Possibly this fact occurred because there were other compounds in the roasted coffee grains, as triacylglycerols, fat acids, caffeine, and others not identified compounds soluble in supercritical CO_2. These compounds extracted in conjunction with these five aromatic compounds, competes to the solvency capacity of the supercritical CO_2, changing the saturation concentration of the solvent. This interaction did not occur when the solubility was measured to the pure compounds. Although the solubility of the pure compound was higher than the same compound in the roasted coffee, the behaviour of the solubility of the 2-methylpyrazine was the same (**Figure 1**), showing a best extraction condition at 55°C. The same behaviour could be observed for 2-furfurylacetate, but the higher solubility was observed at 60°C (**Table 3**).

The solubility for these five pure compounds, and for these same compounds in the roasted coffee showed highest value at determined T, but this T was not coincident for all the compounds, only for 2-methylpyrazine and 2-furfurylacetate. Comparing the solubility of 2-methylpyrazine in roasted coffee at different P (**Table 3**), it was observed that the best value of solubility occurred at 50°C and 275 bar. The same behaviour could be observed for the γ-butyrolactone. **Table 4**, shows the values of the binary interaction parameters (Ka_{ij} and Ka_{ji}) fitting by experimental data of the pure compounds solubilities in supercritical CO_2, using a thermodynamic model that use the Peng-Robinson equation of state. For the binary system furfurylalcohol-supercritical CO_2 (**Figure 2**), it was observed that the biggest deviation between the experimental and calculated data were at 70°C, however both models given good results. The average relative deviation between calculate and experimental values have been practically the same for the two models, 4.34% and 4.42% respectively for the classical and dependent composition mixing rules. Both models also could predict the solubility behavior of the system γ-butyrolactone-supercritical CO_2 (**Figure 3**), pointing a maximum value of solubility, and showing consistency with the experimental data. It was observed that these models presented an relative average deviation between the experimental and calculated solubilities of approximately 6.00%. For these binary system the maximum deviation occurred for the solubility experimental data at 55°C.

CONCLUSION

For these five compounds, the best values of solubility occurred at 275 bar (**Table 3**), and T between 45 and 60°C. Coincidentally, in these operational conditions of P and T were obtained the best yield of the roasted coffee aromatic oil extracted by supercritical CO_2. This results where obtained by a experimental optimisation carried out in a previous study [1]. The model that use

the Peng-Robinson equation of state with the dependent composition mixture rule of Stryjek & Vera [3] adjusted to the experimental data, showing a better prediction. Both thermodynamic models could calculated a maximum point of solubility value only for the γ-butyrolactone-supercritical CO_2 system, showing a solubility behavior like to the experimental data.

ACKNOWLEDGEMENTS

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Table 1. Critical properties and acentric factor of the pure compounds

Compounds	w	T_b (K)		T_c (K)			P_c		
		exp.	A	exp.	A	B	exp.	A	B
CO_2(1)	0,2250		-	304,10	-	-	73,75	-	-
2-methylpyrazine	0,3522	408,20[*]	448,08	-	631,25	603,21	-	53,67	47,51
2-furfurylalcohol	0,7423	443,20[*]	456,38	-	632,55	632,47	-	55,28	49,63
2, 5-dimethylpyrazine	0,3958	428,20[#]	475,34	-	645,94	620,11	-	45,90	40,52
γ-butyrolactone	0,3777	477,70[*]	378,93	731,00[a]	740,43	708,17	51,31[a]	53,82	44,30
2-furfurylacetate	0,5718	450,20[#]	506,25	-	645,83	640,56	-	39,76	34,65

A: [15] [*] Aldrich Chemical Company Inc., 1990 [a] [18]
B: [16] [#] [17]

Table 2. Solubility of the pure compounds in supercritical CO_2 at 250bar (g solute/g CO_2).

T (°C)	2-methylpirazine	2-furfurylalcohol	2,5-dimethylpyrazine	g-butyrolactone	2-furfurylacetate
40	2.3045E-02	2.7273E-02	3.7397E-02	3.8540E-02	2.9182E-02
50	2.6644E-02	3.1981E-02	4.5866E-02	4.1527E-02	4.4674E-02
55	2.9505E-02	3.2942E-02	3.9141E-02	4.9592E-02	4.9032E-02
60	2.6893E-02	3.5604E-02	3.7857E-02	4.3212E-02	5.5345E-02
70	2.6863E-02	3.3287E-02	2.8155E-02	3.9607E-02	5.2601E-02

Table 4. Binary interaction parameters fitting from the experimental data at 250 bar.

Systems	CPARTEST.PAS $Ka_{ij} = Ka_{ji}$	CEPAR2.PAS Ka_{ij}	Ka_{ji}	Temperature (K)	(°C)
2-methylpyrazine supercritical CO_2	0,2530391	0,2149402	-0,0419656	313,15-343,15	40-70
2-furfurylalcohol supercritical CO_2	0,1279375	0,1131269	0,0313026	313,15-343,15	40-70
2,5-dimethylpyrazine supercritical CO_2	0,2217188	0,1862343	-0,0216799	313,15-343,15	40-70
γ-butyrolactone supercritical CO_2	0,1106432	0,1251078	0,2531056	313,15-343,15	40-70
furfurylacetate supercritical CO_2	0,1806770	0,1939286	0,4641417	313,15-343,15	40-70

CPARTEST.PAS: Mixing rule of van der Waals (1890); **CEPAR2.PAS:** Stryjek & Vera [3]

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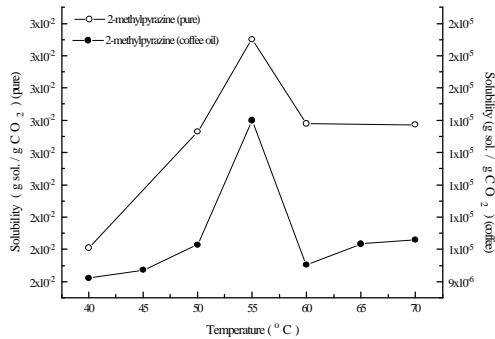
Figure 1. Solubility of 2-methylpyrazine pure, and in the roasted coffee aromatic oil
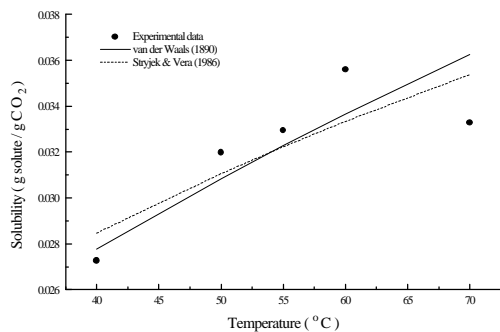
Figure 2. Binary system furfurylalcohol-supercritical CO_2, calculated and experimental data at 250 bar.
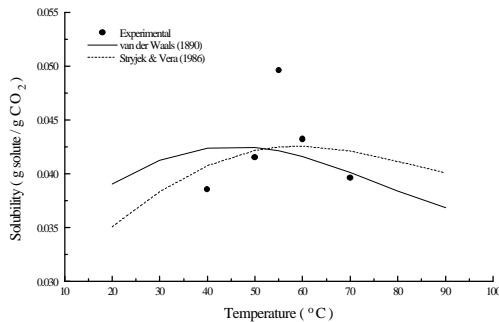
Figure 3. Binary system γ-butyrolactone-supercritical CO_2, calculated and experimental data at 250 bar.

Table 3. Solubility of the five compounds in roasted coffee aromatic oil in supercritical CO_2 (g solute/g CO_2).

	250 (bar)	275 (bar)		300 (bar)	
T (°C)	Solubility (g solute/g CO_2)	Solubility (g solute/g CO_2)	Deviation (%)	Solubility (g solute/g CO_2)	Deviation (%)
2-methylpyrazine					
40	9.1035E-6	9.8907E-6	-	9.6082E-6	-
45	9.3599E-6	7.8365E-6	-	9.1794E-5*	13.51
50	1.0136E-5	2.9213E-5	-	1.2843E-5	-
55	1.3992E-5	1.0248E-5*	11.78	1.7335E-5	-
60	9.5211E-6	1.1138E-5	-	1.1837E-5	-
65	1.0165E-5	1.4079E-5	-	9.9676E-6	-
70	1.0292E-5	4.1546E-6	-		-
2-furfurylalcohol					
40	1.2489E-4	1.0065E-4	-	1.4295E-4	-
45	1.2486E-4	1.2768E-4	-	1.4042E-4*	5.97
50	1.2621E-4	2.9039E-4	-	2.4600E-4	-
55	1.3056E-4	1.5371E-4*	6.04	1.6297E-4	-
60	1.5397E-4	1.5938E-4	-	1.9119E-4	-
65	1.5919E-4	1.4453E-4	-	1.3848E-4	-
70	1.0604E-4	9.4451E-5	-	1.3616E-4	-
2,5-dimethylpyrazine					
40	4.5187E-6	3.9450E-6	-	7.2005E-6	-
45	6.0135E-6	4.8796E-6	-	7.2346E-6*	15.59
50	5.8621E-6	2.5060E-5	-	1.4115E-5	-
55	1.7820E-5	7.4616E-6*	13.01	1.7535E-5	-
65	1.8627E-5	1.7610E-5	-	7.5629E-6	-
70	8.0552E-6	7.2797E-6	-	7.1428E-6	-
		3.4952E-6	-	7.1965E-6	-
g-butyrolactone					
40	2.2605E-5	3.4877E-5	-	2.6232E-5	-
45	3.5997E-5	5.3718E-5	-	5.5643E-5*	2.29
50	3.6505E-5	6.9024E-5	-	6.6623E-5	-
55	3.6747E-5	6.5030E-5*	3.89	4.8628E-5	-
60	4.4954E-5	3.8294E-5	-	3.6810E-5	-
65	3.8666E-5	3.4674E-5	-	3.6291E-5	-
70	3.6600E-5	3.4520E-5	-	3.0849E-5	-
2-furfurylacetate					
40	1.4195E-5	1.6097E-5	-	1.6215E-5	-
45	1.4986E-5	3.5088E-5	-	1.5251E-5*	0.35
50	1.7877E-5	3.5716E-5	-	2.6850E-5	-
55	2.7348E-5	1.7138E-5*	7.73	2.6917E-5	-
60	3.3627E-5	1.6089E-5	-	1.6076E-5	-
65	3.1003E-5	1.6417E-5	-	1.5309E-5	-
70	2.9239E-5	1.4649E-5	-	1.5577E-5	-

$Deviation (\%) = \dfrac{|s|}{Average} \times 100$; *Arithmetic average of three measurements.