THERMODYNAMIC MODELING OF HIGH-PRESSURE PHASE EQUILIBRIA FOR THREE ESSENTIAL OIL+CARBON DIOXIDE SYSTEMS

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In this work, the thermodynamic modeling of high-pressure phase equilibrium data of essential oils present in three odoriferous plants (clove buds, eucalyptus and *Lippia sidoides*) in carbon dioxide is presented. The proposed estimation method uses the volatile oil composition obtained by supercritical fluid extraction for modeling solid-vapor equilibria (SVE). Based on the chemical composition of the volatile oil and using a group contribution method, a pseudo component is defined. The thermodynamic model combines the cubic Peng-Robinson equation of state (PR-EOS) with the van der Waals (VDW), Non-Quadratic Generalized (NQG) and Wong-Sandler-UNIQUAC (WS-UNIQUAC) mixing rules. The fugacity coefficient is obtained numerically by differentiating the pressure with respect to the mole numbers, allowing the combination of any EOS with any mixing rule and eliminating the need for the cumbersome analytical determination. Parameter estimation is performed by using a modified Marquardt method with an objective function that includes the gas phase concentration. The results demonstrate that, in spite of the simplifying assumptions, the model quantitatively describes the experimental data.

INTRODUCTION

The worldwide energy crises and the costumer's choice for natural products have stimulated the search for new technologies. Supercritical fluid extraction (SFE) is known as a clean technology because it presents no harm to either man or the environment. SFE using CO_2 requires no additional treatment of the product and the residues, since the solvent is not toxic. In addition, due to the use of relatively low temperatures, the solute maintains its original characteristics [1].

For the process design of SFE of essential oils from odoriferous plants, reliable methods to calculate the phase equilibrium parameters of the extraction step (plant + CO_2) and the separation step (volatile oil + CO_2) must be available. The volatile oil is a multicomponent mixture composed of very different substances, such as aldehydes, alcohols, terpenes, sesquiterpenes, oxygenated and phenolic compounds, etc. Such systems have a behavior that is appreciably far from the ideal. In addition, the strong asymmetry of the system due to differences of size and polarity of the substances, and the proximity of the solvent critical point require thermodynamic modeling of the SVE using a complex EOS. This would need a considerable amount of experimental data, not yet available. Therefore, simplified models are currently used to assess some information of the system. This work proposes a model for the solubility of three essential oil + CO_2 systems, combining the PR-EOS with several mixing rules. The oils were extracted from three odoriferous plants: clove buds (*Eugenia caryophyllus*), eucalyptus (*Eucalyptus tereticomis* Smith), and *Lippia sidoides* Cham.. The solubility data for these binary systems were obtained using the dynamic method [2].

CHARACTERIZATION OF THE VOLATILE OIL

Volatile oils are multicomponent mixtures composed of substances from several chemical classes, for which the thermophysical properties are mostly unknown. In this work, the entire volatile oil was considered a pseudo-component. The composition of these multicomponent mixtures were obtained by gas chromatography coupled to mass spectrometry [3,4]. The thermophysical properties of CO_2 and some volatile oil components were obtained from AIChE-DIPPR [5]. When the thermophysical properties of the substances were missing, their values were estimated using the group contribution method de Joback [6]. The vapor pressures were estimated using the modified Wagner equation [7]. Once the thermophysical properties of each compound were known, the Kay rule [8] was used to calculate the pseudo-component properties.

THERMODYNAMIC MODEL AND MIXING RULES

In general, the solubility of a solid solute in a supercritical solvent can be derived from the condition of equal fugacities in both phases and represented by:

$$y_i = \frac{P_i^S}{P}\left(\frac{1}{f_i^V}\right)\exp\left[\frac{v_i^S(P - P_i^S)}{RT}\right] \tag{1}$$

where P_i^S is the vapor pressure of solid component, v_i^S is the solid molar volume, P and T are the system pressure and temperature, and ϕ_i^V is the fugacity coefficient of the solute in the supercritical fluid phase. In all calculations, the PR-EOS [9] was used, given by:

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)} \tag{2}$$

I. CLASSICAL vDW AND NQG MIXING RULES

The energy parameter, a, is given by:

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{3}$$

where the cross parameter, a_{ij}, is given by the combination rule:

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \tag{4}$$

For the classical Van der Waals (vDW) mixing rule, k_{ij} is constant. For the Non Quadratic Generalized (NQG) mixing rule [10], k_{ij} depends on concentration in the form:

$$k_{ij} = x_i \boldsymbol{\sigma}_{ij} + x_j \boldsymbol{\sigma}_{ji} \tag{5}$$

with x_i being the mole fraction of component i and σ_{ij} and σ_{ji} being empirical parameters. This rule for the energy parameter a can be considered as a general case, where the well-known Panagiotopoulos and Reid [11] and Adachi and Sugie [12] mixing rules, among others, are special cases. The model takes advantage of the good characteristics of the above mentioned models, allowing more flexibility for the correlation of the experimental data. The proposed model can be reduced to anyone of the above cited models by a correct choice of parameters. The volume parameter, b, is calculated from:

$$b = \sum_i x_i b_i \tag{6}$$

Here, a_i and b_i are pure component parameters.

II. WONG-SANDLER (WS) – UNIQUAC MIXING RULE

The original WS mixing rule, based on the excess Helmholtz free energy, is given by

$$b = \frac{\displaystyle\sum_i\sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij}}{1 - \dfrac{A_\infty^E}{\Theta RT} - \displaystyle\sum_i x_i \frac{a_i}{RTb_i}} \qquad\qquad a = b\left(\sum_i x_i \frac{a_i}{b_i} + \frac{A_\infty^E}{\Theta RT}\right) \tag{7}$$

where Θ is a constant that depends of the EOS (for the PR EOS: $\Theta = \ln(\sqrt{2}-1)/\sqrt{2}$) and A_∞^E/RT is calculated from UNIQUAC model. The cross virial coefficient was modified by Orbey and Sandler [13] and is given by:

$$\left(b - \frac{a}{RT}\right)_{ij} = \left(\frac{b_i + b_j}{2}\right) - \frac{\sqrt{a_i a_j}}{RT}\left(1 - k_{ij}\right) \tag{8}$$

where k_{ij} is the binary interaction parameter, a_i and b_i are pure component parameters.

NUMERICAL CALCULATION OF THE FUGACITY COEFFICIENT

For any mixing rule, the fugacity coefficient, ϕ_i, required for phase equilibrium calculations, is calculated from exact thermodynamic relationship given by Prausnitz [14].

$$\ln f_i = \frac{1}{RT}\int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{i\neq j}} - \frac{RT}{V}\right]dV - \ln Z \tag{9}$$

In this work, the fugacity coefficient is obtained by numerical differentiation of the pressure with respect to the mole numbers of respective component and then integrating eqn. (9). This differentiation allows the combination of any EOS with any mixing rule and eliminates the need for the cumbersome analytical determination of this property.

$$\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{i\neq j}} = \frac{P(T,\underline{V}',x') - P(T,\underline{V}'',x'')}{2(n_i' - n_i'')} \tag{10}$$

where: x' and x'' are the perturbed composition vectors, V is absolute volume and $\underline{V}$ is the molar volume.

RESULTS

Table 1 shows the thermophysical properties of the volatile oils, obtained by Sousa [1].

Table 1: Thermophysical properties of clove oil, eucalyptus oil, and L. sidoides oil

Volatile Oil	MW (g/mol)	Tb (K)	Tc (K)	Pc (bar)	ω	A_p*	B_p*
Clove	172.38	530.11	737.60	32.44	0.6397	1.4254	-0.0014
Eucalyptus – NE	184.00	541.31	762.38	24.93	0.4435	1.4897	-0.0017
L. Sidoides	159.66	533.24	755.71	30.90	0.5145	1.3933	-0.0015

* ρ (g/cm^3) = Ap + Bp.T (K), from 283 to 298 K

Table 2 reports estimated values of the binary interaction parameters obtained in the modeling of the solubility of essential oils in CO_2. Several models of mixing rule and binary interaction parameter were studied. In cases I [1] and II (this work), k_{ij} remains constant. In case III, k_{ij} varies lineally with temperature. In case IV, k_{ij} varies inversely proportional to temperature. In all these cases, the model was the vDW mixing rule. In case V, the binary interaction parameter, k_{ij}, depends on the concentration. This case corresponds to the Non Quadratic Generalized mixing rule, NQG [10]. In case VI, the WS-UNIQUAC mixing rule was applied for optimizing the binary interaction parameter, k_{ij}, and its own parameters (τ_{ij}, τ_{ji}). In all

cases, the PR-EOS was used to modeling the high pressure phase equilibria of these binary systems.

Table 2: Interaction parameters for modeling of solubilities of essential oils in CO_2.

case	mixing rule	interaction parameter		CO_2 +		
				clove oil	L. sidoides oil	eucalyptus oil
I		k_{ij} = cte		0.019	0.234	0.2960
II		k_{ij} = cte		0.2164	0.4236	0.5773
III	vDW	k_{ij} = A + B*T	A	-0.1592	0.2812	0.4912
			B	0.0013	0.0005	0.0003
IV		k_{ij} = A + B/T	A	0.4962	0.4921	0.2714
			B	-81.7045	-19.3251	88.7152
V	NQG	$k_{ij} = \sigma_{ij}.x_i + \sigma_{ji}.x_j$	σ_{ij}	0.1023	0.1852	0.1972
			σ_{ji}	0.6981	-0.1013	0.4128
VI	WS-UNIQUAC	k_{ij}		-0.2854	-0.1421	-0.8741
		τ_{ij} (cal/mol.K)		205.36	652.12	821.36
		τ_{ji} (cal/mol.K)		453.21	400.41	450.36

The parameter estimation is performed by using the modified Marquardt method [15] and an objective function including the oil and CO_2 vapor phase concentrations.

$$OF = \sum_{1}^{NP}\left[\left|\frac{y_{1,i}^{\exp} - y_{1,i}^{calc}}{y_{1,i}^{\exp}}\right| + \left|\frac{y_{2,i}^{\exp} - y_{2,i}^{calc}}{y_{2,i}^{\exp}}\right|\right]*100 \qquad (11)$$

where NP is the number of experimental data, 1 represents the CO_2 and 2 represents the volatile oil.. Tables 3, 4, and 5 report the estimated values of solubilities for modeling of essential oils in carbon dioxide and the relative and mean deviations. These deviations were calculated by: $\left(\left(y_2^{\exp} - y_2^{calc}\right)/ y_2^{\exp}\right)*100$.

Table 3: Solubilities for the SVE for the binary system: CO_2 (1) + clove oil (2)

Exp. Data	P (bar)	T (K)	Solubility ($y_2 * 10^2$)							Relative deviation (%)					
			Exp	Calculated						I	II	III	IV	V	VI
				I	II	III	IV	V	VI						
[1]	66.7	283.15	6.18	7.46	5.11	5.55	5.41	5.80	5.34	20.71	17.30	10.12	12.50	6.21	13.58
	66.7	288.15	6.25	5.55	5.58	5.63	5.58	6.24	6.21	11.20	10.70	9.92	10.77	0.20	0.64
[7]	66.0	288.15	5.36	5.48	5.56	5.61	5.56	5.46	5.32	2.24	3.80	4.71	3.72	1.85	0.75
	70.0	288.15	5.61	5.86	5.66	5.71	5.66	5.70	5.54	4.46	0.88	1.77	0.80	1.53	1.25
	72.0	288.15	5.73	6.04	5.70	5.75	5.70	5.76	5.63	5.41	0.46	0.42	0.53	0.54	1.75
	80.0	288.15	5.86	6.75	5.86	5.91	5.86	6.00	5.81	15.19	0.00	0.88	0.07	2.36	0.85
	100.0	298.15	6.38	5.14	7.20	6.37	6.54	6.40	6.28	19.44	12.83	0.16	2.52	0.36	1.57
								Mean Deviation		11.23	6.57	400	4.42	1.86	2.91

Table 4: Solubilities for the SVE for the binary system: CO_2 (1) + L. sidoides oil (2)

Exp. Data	P (bar)	T (K)	Solubility (y_2*10^2)							Relative deviation (%)					
			Exp	Calculated						I	II	III	IV	V	VI
				I	II	III	IV	V	VI						
[1]	66.7	288.15	0.53	0.50	0.38	0.37	0.38	0.54	0.48	5.66	28.79	29.30	27.87	1.91	9.39
	66.7	293.15	0.62	0.50	0.47	0.45	0.47	0.58	0.51	19.35	24.43	27.66	24.77	6.43	18.35
[7]	66.7	295.65	0.52	0.47	0.52	0.49	0.51	0.55	0.52	9.62	0.05	5.83	1.18	5.80	0.07
	66.7	283.15	0.36	0.47	0.30	0.31	0.31	0.37	0.46	30.56	16.30	13.56	13.55	3.74	26.44
	66.7	298.15	0.36	0.42	0.58	0.53	0.57	0.37	0.43	16.67	60.14	48.30	56.98	3.74	20.04
	78.5	288.15	0.49	0.51	0.46	0.46	0.47	0.67	0.50	4.08	6.31	6.99	4.97	37.51	1.22
	78.5	293.15	0.55	0.53	0.58	0.55	0.58	0.67	0.52	3.64	4.91	0.45	4.57	22.51	4.89
								Mean Deviation		12.80	20.13	18.87	19.13	11.66	11.49

Table 5: Solubilities for the SVE for the binary system: CO_2 (1) + eucalyptus oil (2)

Exp. Data	P (bar)	T (K)	Solubility (y_2*10^3)							Relative deviation (%)					
			Exp	Calculated						I	II	III	IV	V	VI
				I	II	III	IV	V	VI						
[1]	66.7	288.15	0.94	0.89	0.94	0.94	0.94	0.93	0.82	5.32	0.09	0.28	0.02	0.58	12.67
	66.7	288.15	0.98	0.89	0.94	0.94	0.94	0.95	0.82	9.18	4.17	4.35	4.10	3.55	16.23
	66.7	283.15	0.49	0.64	0.67	0.69	0.63	0.61	0.47	30.61	37.71	40.34	27.68	24.73	4.73
	66.7	293.15	0.97	1.20	1.29	1.26	1.38	1.17	1.00	23.71	32.76	30.00	42.13	20.66	3.01
	78.5	288.15	1.18	0.82	0.97	0.96	0.95	1.06	0.95	30.51	18.10	18.28	19.49	10.45	19.71
							Mean Deviation			19.87	18.56	18.65	18.68	12.00	11.27

The results are analyzed in terms of mean deviations in oil vapor composition. For the classical rules, the vDW form shows the highest deviations in oil vapor composition. Cases I and II, where binary interaction parameter remains constant, show highest deviations for this mixing rule. When k_{ij} depends on temperature (cases III and IV) the deviations decrease. The NQG and WS-UNIQUAC mixing rules show the lowest deviations in oil vapor composition for the three essential oils. The dispersion between calculated and experimental values of the solubility for the three cases can be seen in Figures 1, 2 and 3.
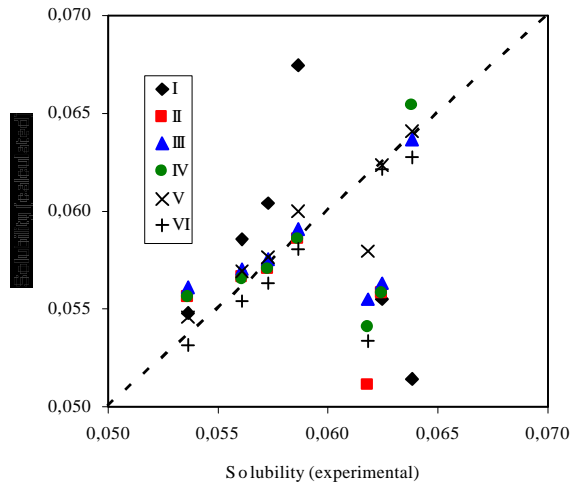

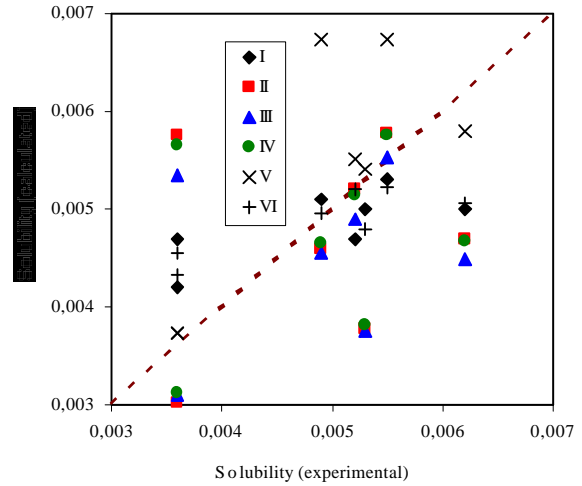Figure 1. Solubility of clove oil in CO_2
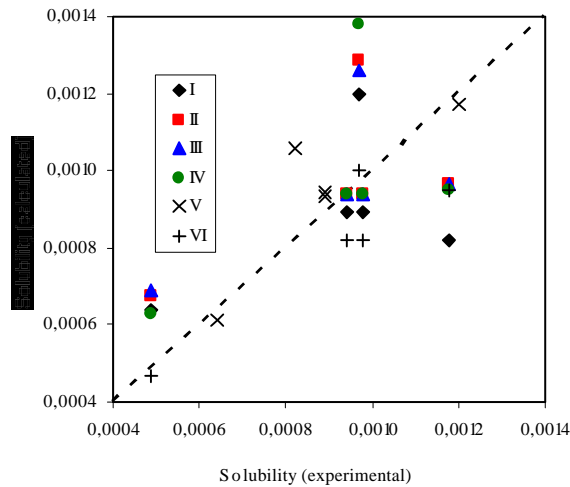

Figure 2. Solubility of L. sidoides oil in CO_2

Figure 3. Solubility of eucalyptus oil in CO_2

CONCLUSION

Solid-vapor equilibrium data for three complex binary mixtures de CO_2 + essential oils have been correlated using the PR EOS with the vDW, NQG and WS-UNIQUAC mixing rules.

The methodology employed to estimate the solubility of essential oils in CO_2 provided satisfactory results, despite the simplifications made to treat the entire volatile oil as a pseudo component. The dependence on composition of the binary interaction parameter, k_{ij}, for the NGQ mixing rule improves the precision of calculations. However, the WS-UNIQUAC mixing rule gives the best results.

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