**Correlating the solubility of supercritical gases in high molecular
weight substances using a density-dependent equation**

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Abstract

Chrastil (1982) established that the solubility of a substance in a supercritical fluid can be correlated with the density of the pure supercritical gas. Recently, the solubility of supercritical fluids in different organic liquids was successfully correlated as a function solely of the supercritical fluid density, since we demonstrated that the supercritical fluid density also defines the solubility of the gas in the liquid phase.

In this work, the solubility of supercritical carbon dioxide in high molecular weight substances, such as high molecular weight paraffins, alcohols, fatty acids, fatty acid methyl and ethyl esters, has been correlated and constants provided. More than 20 binary systems comprising around 1000 solubility data points were correlated, obtaining regression coefficients greater than 0.96 and confirming the goodness of the density-dependent equation previously reported.

Keywords: solubility; supercritical fluids; vapor-liquid equilibria; Chrastil equation.

Introduction

Stahl et al.¹ firstly observed a close relationship between the solubility of a substance and the supercritical solvent density. In 1982, Chrastil² presented an equation based on the solvato complex model, which establishes a linear dependency, in logarithmic basis, between the solute solubility and the supercritical fluid density (ρ_{SCF}). That is, a simple density-dependent equation was capable to correlate the equilibrium composition (i.e. the solubility) of a solute in the high pressure vapor phase of binary vapor-liquid or vapor-solid equilibria. Chrastil's equation was found to be applicable for dilute gas solutions (i.e. low concentration of solute in the supercritical phase) and thus, was widely employed to correlate the solubility of high molecular weight substances in supercritical carbon dioxide³⁻⁶ (SCCO₂).

On the other side, the solubility of a gas in a liquid was conventionally described using Henry's law, which establishes that the amount of gas dissolved in a liquid is linearly proportional to its partial pressure. This law was found to be accurate for dilute liquid solutions (i.e. low amounts of gas dissolved in the liquid phase). As concentration or pressure increase, deviations from Henry's law become noticeable. Thus, this law is usually not capable to represent the solubility of a supercritical fluid in organic liquids. At high pressures, mixtures of CO₂ + low molecular weight substances exhibit, in general, positive deviations to Henry's law while mixtures of CO₂ + high molecular weight substances typically present negative deviations.

In a previous contribution⁷, we demonstrated that not only the composition of the vapor phase, as Chrastil² established, but also the composition of the liquid phase is simply related with the SCF density. The solubility of a supercritical gas in a liquid (i.e. the SCF molar fraction in the liquid phase, X_{SCF}) was straightforwardly correlated with ρ_{SCF} . Two semi-empirical density-dependent equations were presented which proved to

be valid for mixtures presenting, respectively, positive and negative deviations to Henry's law. In this work, the corresponding correlative constants are given to represent the solubility of SCCO₂ in certain high molecular weight substances usually involved in technological applications of supercritical fluid processing.

Theoretical background

High pressure solubility of solutes in supercritical gases: Chrastil's equation.

At constant temperature, the relationship between the solute solubility and the supercritical solvent density was established as follows:

$$\ln S_s = k' \ln(\rho_{SCF}) + b' \quad (\text{constant temperature}) \quad (1)$$

S_s is the solute solubility (g/L), ρ_{SCF} is the density of the pure supercritical gas (g/L) and k' and b' are semi-empirical parameters.

As mentioned before, Eq. (1) was broadly employed in the literature to correlate the solubility of many compounds in supercritical gases, particularly in SCCO₂. For example, Güçlü-Üstündag and Temelli^{3,4} reported k' and b' parameters for a large set of lipid-type substances.

Solubility of supercritical fluids in organic liquids.

In a previous work⁷ and based on a modification of Henry's law, we presented two semi-empirical density-dependent correlations to represent the solubility of a supercritical fluid in a liquid.

The SCF molar fraction in the liquid phase (X_{SCF}) was given by the following relationship:

$$\ln(X_{SCF}) = A \cdot \ln(\rho_{SCF}) + B \quad (\text{constant temperature}) \quad (2)$$

for binary mixtures which exhibit positive deviations to Henry's law, that is, when $X_{SCF} > K_H P_{SCF}$, being P_{SCF} the gas partial pressure and K_H Henry's constant.

In Eq. (2), A and B are constants which are regressed from X_{SCF} experimental data, and ρ_{SCF} is the SCF density given in kg/m^3 .

The validity of Eq. (2) was demonstrated in previous work⁷ employing a large and varied set of vapor-liquid equilibria data including different organic liquids (alkanes, alkenes, alcohols, acids, ketones, esters, terpenes and aromatic compounds). The linear regression coefficients (R^2) obtained when applying Eq. (2) to correlate $\ln(X_{SCF})$ vs. $\ln(\rho_{SCF})$ were greater than 0.98 when the mixtures exhibit positive deviations to Henry's law, but quite lower R^2 values were obtained in the case of mixture with negative deviations.

As mentioned before, most attractive applications of supercritical processes are related with high molecular weight substances, which in general exhibit negative deviations to Henry's law. Thus, Eq. (2) was empirically modified as follows:

$$\ln X_{SCF} = A^* \frac{\ln(\rho_{SCF})}{P} + B^* \quad (\text{constant temperature}) \quad (3)$$

where P is the pressure (MPa), ρ_{SCF} the supercritical fluid density (kg/m^3) and A^* and B^* are the correlative constants which are regressed from experimental data. Eq. (3) establishes a linear relationship between $\ln(X_{SCF})$ and $\ln(\rho_{SCF})/P$ and was successfully applied to various binary mixtures of CO_2 + high molecular weight substances⁷.

Results and discussion

Regression coefficients obtained for the systems studied.

Eq. (3) was used to correlate the solubility of SCCO_2 in substances comprising certain families of compounds which are particularly interesting in supercritical CO_2

processing. Tables 1 to 5 present the different systems investigated: high molecular weight paraffins (Table 1), high molecular weight alcohols (Table 2), fatty acids (Table 3), fatty acid methyl esters (Table 4) and fatty acid ethyl esters (Table 5). Also given in the tables are the source of the experimental solubility data employed⁸⁻²³, the values of constants A^* and B^* obtained and the R^2 values resulted from the regression procedure.

As can be observed in the tables the R^2 values obtained when employing Eq. (3) to correlate the solubility of CO₂ in high molecular weight alkanes and alcohols were greater than 0.97. Figure 1 depicts the quality of the regression achieved for some selected *n*-alkanes and *n*-alcohols.

High regression coefficients were also obtained in the case of fatty acids (see Table 3) and fatty acid alkyl esters (Tables 4 and 5). As example, Figure 2 show the linear behavior obtained between $\ln(X_{CO_2})$ vs. $\ln(\rho_{CO_2})/P$ for some selected CO₂ + fatty acid methyl ester mixtures.

In general, lower R^2 values resulted when merging in the regression procedure the solubility data reported by different authors. For example, the solubility of CO₂ in methyl oleate at 333 K was correlated obtaining R^2 values of 0.954, 0.997 and 0.967 when the data reported, respectively, by Zou et al.¹⁵, Yu et al.¹⁶ and Chang et al.²⁰ were separately considered. On the other hand, when the three sources of data were taken into account simultaneously, the R^2 obtained was somewhat lower (0.920). Similar results were obtained for other systems studied (see Tables 3 to 5). This is quite reasonable to expect due to the different equipments and procedures employed in the experimental determinations, which can produce systematic differences between the data reported. For example, in the case of the CO₂ + oleic acid mixture at 313 K, the R^2 values obtained considering separately the different sources of solubility data available¹⁴⁻¹⁶ were quite satisfactory but when merging all the experimental data available a quite

poorer regression resulted ($R^2 = 0.826$). Figure 3 shows that this result should be attributed to the high discrepancies found between the experimental data reported at 313 K and not to a failure of Eq. (3) to correlate the CO₂ solubility data. Actually, considering the same system (CO₂ + oleic acid) and the same sources of experimental data¹⁴⁻¹⁶ but a different temperature (333 K), the R^2 values obtained were higher than 0.950 considering separately each source of solubility data or merging the data all together in the regression procedure (see Table 3).

Comparison between the density-dependent correlation (Eq. 3) and the GC-EoS model in the calculation of CO₂ solubility in high molecular weight substances.

The liquid phase composition of the CO₂ + high-molecular weight systems referred in Tables 1 to 5 were calculated using two different approaches: the density-dependent correlation given by Eq. (3) and the Group Contribution Equation of State (GC-EoS) model developed by Skjold-Jørgensen²⁴.

Parameters A^* and B^* employed when applying Eq. (3) to calculate X_{CO_2} were those regressed in this work and are given in the corresponding tables.

With respect to the GC-EoS model, which is based on the group contribution approach, the reader is referred to the work of Fornari²⁵ where all pure group and binary group interaction parameters required (i.e. those corresponding to the CO₂, -CH₃, -CH₂, -CH₂OH, -COOCH₃ and -COOCH₂- groups) are given. Pure component parameters, i.e. critical temperature (T_c), critical pressure (P_c) and critical hard sphere diameter (d_c) are given in Table 6 for some of the high molecular weight substances studied. For high size-asymmetric mixtures, the d_c parameter of the high molecular weight compound greatly affects the GC-EoS phase composition calculations²⁵. Thus, this parameter was optimized in this work (see Table 6) in order to minimize the average absolute

deviations (*AAD*) between the experimental and calculated CO₂ liquid mole fraction.

The *AAD*% values are calculated as follows:

$$AAD\% = (100/N_{\text{exp}}) \sum |x_{CO_2}^{\text{exp}} - x_{CO_2}^{\text{cal}}| / x_{CO_2}^{\text{exp}} \quad (4)$$

In this way, the best GC-EoS correlation of the X_{CO_2} data that could be achieved is compared with Eq. (3) correlation.

Table 7 gives the *AAD*% resulted. As can be deduced from the table, Eq. (3) produce *AAD*% values lower (or of the same order of magnitude) than those resulted when applying the GC-EoS model in a correlative manner.

Conclusions

In this work, a Chrastil-type equation was applied to correlate the solubility of SCCO₂ (i.e. the CO₂ molar fraction, X_{CO_2}) in high molecular weight liquid substances as a function of solely the CO₂ density (ρ_{CO_2}). Based on experimental X_{CO_2} data from the literature, the parameters of the linear correlation between $\ln(X_{CO_2})$ and $\ln(\rho_{CO_2})/P$ were given for 26 different substances comprising *n*-alkanes, *n*-alcohols, fatty acids and fatty acid alkyl (methyl and ethyl) esters. High linear regression coefficients were obtained for all systems studied, confirming the goodness of the density-dependent equation employed.

This new correlation permits the calculation of binary CO₂ + substance liquid phase composition, circumventing the use of EoS based models (which are not always available or comprehensible for many people working in supercritical fluid processing) and with similar accuracy. Although this approach could never substitute the role of EoS models for process simulation, the correlation presented in this work provide a simple, fast and accurate manner to calculate the solubility of a supercritical fluid in a liquid.

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Literature cited

1. Stahl E, Schilz W, Schütz E, Willing E. A quick method for the microanalytical of the dissolving power of supercritical gases. *Angew. Chem., Int. Ed. Engl.* 1978; 17:731-738.
2. Chrastil J. Solubility of solids and liquids in supercritical gases. *J. Phys. Chem.* 1982; 86:3016-3021.
3. Güçlü-Üstündag Ö, Temelli F. Correlating the solubility behavior of fatty acids, mono-, di-, and triglycerides, and fatty acid esters in supercritical carbon dioxide. *Ind. Eng. Chem. Res.* 2000; 39:4756-4766.
4. Güçlü-Üstündag Ö, Temelli F. Correlating the solubility behavior of minor lipid components in supercritical carbon dioxide. *J. Supercrit. Fluids* 2004; 31:235-253.
5. Setianto WB, Nawi AH, Ab. Kadir MO. Application of Chrastil Model to the Virgin Coconut and Palm Kernel Oil Solubility in Supercritical Carbon Dioxide. International Conference on Environmental Research and Technology (ICERT). Cleaner tech, control, treatment & remediation technique, pp. 921-925, 2008.
6. Del Valle JM, Aguilera JM. An improved equation for prediction the solubility of vegetable oils in supercritical CO₂. *Ind. Eng. Chem. Res.* 1988; 27:1551-1553.
7. Fornari T, Hernández EJ, Reglero G. Solubility of supercritical gases in organic liquids. *J. Supercrit. Fluids*, in press.
8. Charoensombut-amon T, Martin RJ, Kobayashi R. Application of a generalized multiproperty apparatus to measure phase equilibrium and vapor phase densities of supercritical carbon dioxide in n-hexadecane systems up to 26 MPa. *Fluid Phase Equilib.* 1986; 31:89-104.
9. Sebastian HM, Simnick JJ, Lin H-M, Chao K-C. Vapor-liquid equilibrium in binary mixtures of carbon dioxide + n-decane and carbon dioxide + n-hexadecane. *J. Chem. Eng. Data* 1980; 25:138-140.
10. Nieuwoudt I, du Rand M. Measurement of phase equilibria of supercritical carbon dioxide and paraffins. *J. Supercrit. Fluids* 2002; 22:185-199.
11. Sato Y, Tagashira Y, Maruyama D, Takishima S, Masuoka H. Solubility of carbon dioxide in eicosane, docosane, tetracosane, and octacosane at temperatures from 323 to 473 K and pressures up to 40 MPa. *Fluid Phase Equilibria* 1998; 147:181-193.

12. Chang CJ, Chiu K-L, Day C-Y. A new apparatus for the determination of P - x - y diagrams and Henry's constants in high pressure alcohols with critical carbon dioxide. *J. Supercrit. Fluids* 1998; 12:223-237.
13. Jan D-S, Mai C-H, Tsai F-N. Solubility of Carbon Dioxide in 1-Tetradecanol, 1-Hexadecanol, and 1-Octadecanol. *J. Chem. Eng. Data* 1994; 39:384-387.
14. Bharath R, Inomata H, Adschiri T, Arai K. Phase equilibrium study for the separation and fractionation of fatty oil components using supercritical carbon dioxide. *Fluid Phase Equilibria* 1992; 81:307-320.
15. Zou M, Yu ZR, Kashulines P, Rizvi SSH, Zollweg J. A. Fluid-liquid phase equilibria of fatty acids and fatty acid methyl esters in supercritical carbon dioxide. *J. Supercrit. Fluids* 1990; 3:23-28.
16. Yu ZR, Rizvi SSH, Zollweg J. A. Phase equilibrium of oleic acid, methyl oleate, and anhydrous milk fat in supercritical CO₂. *J. Supercrit. Fluids* 1992; 5:114-122.
17. Inomata H, Kondo T, Hirohama S, Arai K, Suzuki Y, Konno M. Vapour-liquid equilibria for binary mixtures of carbon dioxide and fatty acid methyl esters. *Fluid Phase Equilibria* 1989; 46: 41-52.
18. Lockeman CA, Muñoz de Soto-Soliz S, Schlünder EU. High-pressure phase equilibria and densities of the binary system carbon dioxide/methyl laurate. *Chemical Engineering and Processing* 1995; 34:561-564.
19. Lockemann CA. High-pressure phase equilibria and densities of the binary mixtures carbon dioxide-oleic acid, carbon dioxide-methyl myristate, and carbon dioxide-methyl palmitate and of the ternary mixture carbon dioxide-methyl myristate-methyl palmitate. *Chemical Engineering and Processing* 1994; 33: 171- 187.
20. Chang C-MJ, Lee M-S, Li B-C, Chen P-Y. Vapor-Liquid Equilibria of CO₂ with Four Unsaturated Fatty Acid Esters and Their Correlations at Elevated Pressures. *Fluid Phase Equilibria* 2005; 233:56-65.
21. Hwu W-H, Cheng J-S, Cheng K-W, Chen Y-P. Vapor-Liquid Equilibrium of Carbon Dioxide with Ethyl Caproate, Ethyl Caprylate and Ethyl Caprate at Elevated Pressures. *J. Supercrit. Fluids* 2004; 28:1-9.
22. Bharath R, Inomata H, Arai K, Shoji K, Noguchi Y. Vapor-liquid equilibria for binary mixtures of carbon dioxide and fatty acid ethyl esters. *Fluid Phase Equilibria* 1989; 50:315-327.

23. Jaubert J-N, Borg P, Coniglio L, Barth D. Phase equilibria measurements and modeling of EPA and DHA ethyl esters in supercritical carbon dioxide. *J. Supercrit. Fluids* 2001; 20:145-155.
24. Skjold-Jørgensen S. Group Contribution Equation of State (GC-EOS): A Predictive Method for Phase Equilibrium Computations over Wide Ranges of Temperatures and Pressures up to 30 MPa. *Ind. Eng. Chem. Res.* 1988; 27:110-118.
25. Fornari T. Revision and summary of the group contribution equation of state parameter table: Application to edible oil constituents. *Fluid Phase Equilibria* 2007; 262:187-209.
26. Joback KG, Reid RC. Estimation of pure-component properties from group contributions. *Chem. Eng. Commun.* 1983; 57:233- 243.

Table 1. Parameters A^* and B^* of Eq. (3) for different CO₂ + high molecular weight alkane binary mixtures. R^2 : linear regression coefficient. P is given in MPa and ρ_{CO_2} in kg/m³.

alkane	T / K	P range / MPa	X_{CO_2} range	ρ_{CO_2} range / kg·m ⁻³	N_{exp}	$-A^*$	B^*	R^2	ref.
hexadecane	313.2	0.69 - 12.25	0.08 - 0.97	12.0 - 725	15	1.3455	0.6600	0.981	8
	323.2	0.69 - 17.00	0.07 - 0.97	11.6 - 740	16	1.2509	0.4394	0.993	8
	333.2	0.69 - 21.73	0.07 - 0.97	11.2 - 749	12	1.2926	0.3526	0.997	8
	343.2	0.69 - 25.82	0.07 - 0.97	10.9 - 747	17	1.2826	0.2787	0.993	8
	462.9	2.00 - 5.08	0.11 - 0.26	23.4 - 61.1	4	1.1215	0.4664	0.997	9
	663.4	2.08 - 5.07	0.09 - 0.25	16.7 - 40.6	4	1.6365	0.2158	0.999	9
eicosane	315.9	7.74 - 24.90	0.77 - 0.86	234 - 868	4	0.2521	0.0818	0.978	10
	320.6	8.64 - 22.31	0.77 - 0.86	274 - 823	4	0.3142	0.0548	0.979	10
	329.6	10.43 - 25.89	0.77 - 0.88	346 - 812	5	0.4287	0.0149	0.975	10
	339.1	10.43 - 24.65	0.77 - 0.88	283 - 754	5	0.4999	0.0066	0.989	10
	348.3	11.50 - 28.79	0.77 - 0.92	295 - 755	5	0.6435	0.0499	0.978	10
tetracosane	357.1	18.50 - 30.16	0.82 - 0.88	528 - 731	5	0.6041	0.0081	0.996	10
	423.2	12.28 - 38.48	0.55 - 0.90	185 - 592	7	1.8522	0.1998	0.997	11

Table 2. Parameters A^* and B^* of Eq. (3) for different CO₂ + high molecular weight alcohol binary mixtures. R^2 : linear regression coefficient. P is given in MPa and ρ_{CO_2} in kg/m³.

alcohol	T / K	P range / MPa	X_{CO_2} range	ρ_{CO_2} range / kg·m ⁻³	N_{exp}	$-A^*$	B^*	R^2	ref.
decanol	308.2	2.23 - 7.75	0.16 - 0.58	42.9 - 320	9	1.3249	0.3257	0.974	12
	318.2	2.18 - 10.47	0.15 - 0.65	40.0 - 559	9	1.3571	0.3119	0.979	12
	328.2	2.89 - 15.17	0.18 - 0.71	52.4 - 659	13	1.5315	0.3136	0.992	12
tetradecanol	373.0	1.01 - 5.07	0.06 - 0.27	14.7 - 81.9	5	0.8122	0.6789	0.985	13
	423.0	1.01 - 5.07	0.06 - 0.25	12.8 - 68.5	5	0.8449	0.7559	0.981	13
	573.0	1.01 - 5.07	0.05 - 0.21	9.4 - 47.6	5	0.9956	0.8824	0.992	13
hexadecanol	373.0	1.01 - 5.07	0.06 - 0.30	14.7 - 82.0	5	0.8594	0.5280	0.985	13
	473.0	1.01 - 5.07	0.05 - 0.24	11.4 - 59.4	5	0.9275	0.7731	0.981	13
	573.0	1.01 - 5.07	0.04 - 0.20	9.4 - 47.6	5	1.0659	0.8316	0.995	13
octadecanol	373.0	1.01 - 5.07	0.07 - 0.29	14.7 - 82.0	5	0.7781	0.6003	0.991	13
	473.0	1.01 - 5.07	0.05 - 0.23	11.4 - 59.4	5	0.884	0.8459	0.991	13
	573.0	1.01 - 5.07	0.05 - 0.21	9.4 - 47.6	5	1.0245	0.8179	0.993	13

Table 3. Parameters A^* and B^* of Eq. (3) for different CO₂ + fatty acid binary mixtures. R^2 : linear regression coefficient. P is given in MPa and ρ_{CO_2} in kg/m³.

fatty acid	T / K	P range / MPa	X_{CO_2} range	ρ_{CO_2} range / $\text{kg} \cdot \text{m}^{-3}$	N_{exp}	$-A^*$	B^*	R^2	Ref.
caproic	313.2	2.76 - 5.29	0.31 - 0.91	53.4 - 347	4	1.2810	0.6652	0.944	14
	353.2	2.72 - 15.88	0.17 - 0.87	44.3 - 464	6	1.5308	0.2808	0.962	14
lauric	333.2	2.57 - 24.64	0.24 - 0.88	45.0 - 783	10	1.0736	0.1496	0.994	14
	353.0	5.33 - 27.65	0.35 - 0.89	95.2 - 721	6	1.5046	0.224	0.997	14
palmitic	353.2	15.36 - 30.52	0.64 - 0.80	443 - 751	3	1.2618	0.0573	0.997	14
	373.2	13.60 - 30.46	0.57 - 0.80	289 - 668	4	1.5005	0.0654	0.967	14
oleic	313.0	7.27 - 28.41	0.66 - 0.81	216 - 826	6	0.4066	0.1111	0.999	15
	313.2	10.17 - 30.00	0.79 - 0.83	642 - 911	5	0.0997	0.1566	0.890	14
	313.2	3.36 - 31.08	0.36 - 0.81	67.3 - 917	9	0.7204	0.0069	0.933	16
	313.0	3.36 - 31.08	0.66 - 0.96	67.3 - 917	20	0.6491	0.0088	0.826	14-16
	333.0	7.10 - 28.80	0.65 - 0.80	159 - 822	6	0.5066	0.1028	0.964	15
	333.2	10.73 - 30.02	0.65 - 0.81	338 - 831	5	0.6408	0.0643	0.994	14
	333.2	6.58 - 31.12	0.51 - 0.82	142 - 839	8	0.8145	0.0069	0.955	16
	333.2	6.58 - 31.12	0.51 - 0.82	142 - 839	19	0.7681	0.0228	0.950	14-16
	353.2	11.06 - 29.34	0.59 - 0.80	259 - 739	5	1.0707	0.0266	0.989	14
	313.0	6.40 - 26.50	0.72 - 0.82	167 - 891	6	0.2209	0.1506	0.991	15
linoleic	333.0	6.34 - 27.14	0.67 - 0.80	135 - 808	6	0.3361	0.145	0.963	15

Table 4. Parameters A^* and B^* of Eq. (3) for different CO₂ + fatty acid methyl esters binary mixtures. R^2 : linear regression coefficient. P is given in MPa and ρ_{CO_2} in kg/m³.

fatty acid methyl ester	T / K	P range / MPa	X_{CO_2} range	ρ_{CO_2} range / kg·m ⁻³	N_{exp}	- A^*	B^*	R^2	ref.
stearate	313.2	2.75 - 13.44	0.50 - 0.93	53.0 - 753	8	0.6529	0.2578	0.976	17
	323.2	2.15 - 16.32	0.45 - 0.93	38.5 - 759	9	0.5894	0.1346	0.943	17
	333.2	5.74 - 17.31	0.57 - 0.90	118 - 672	4	0.9681	0.2596	0.997	17
	343.2	6.18 - 19.73	0.53 - 0.90	121 - 654	6	1.1349	0.2666	0.995	17
laureate	313.0	3.00 - 8.00	0.42 - 0.79	58.9 - 279	6	1.0312	0.5099	0.970	18
	323.0	3.00 - 10.00	0.28 - 0.88	56.0 - 387	8	1.4937	0.7065	0.992	18
	333.0	2.00 - 12.00	0.15 - 0.87	34.2 - 437	11	1.3275	0.4745	0.993	18
myristate	313.2	2.26 - 9.17	0.32 - 0.94	42.5 - 527	8	1.0532	0.5913	0.983	17
	313.0	1.07 - 8.01	0.10 - 0.76	18.9 - 281	9	0.9759	0.3345	0.992	19
	313.0	1.07 - 9.17	0.10 - 0.94	18.9 - 527	17	1.0607	0.5175	0.972	17,19
	323.0	2.21 - 11.65	0.34 - 0.92	39.7 - 562	7	0.8796	0.345	0.983	17
	323.0	0.88 - 9.00	0.14 - 0.94	14.9 - 286	13	0.7517	0.2906	0.989	19
palmitate	323.0	0.88 - 11.65	0.14 - 0.94	14.9 - 562	20	0.7577	0.2783	0.982	17, 19
	313.2	2.48 - 11.10	0.40 - 0.95	47.2 - 288	12	0.9019	0.4496	0.980	17
	313.0	1.22 - 10.00	0.19 - 0.91	21.7 - 633	11	0.8018	0.3526	0.989	19
	313.0	1.22 - 11.10	0.19 - 0.95	21.7 - 633	23	0.8264	0.3816	0.985	17, 19
	323.0	2.12 - 13.49	0.33 - 0.92	37.9 - 656	7	0.8286	0.2787	0.984	17
	323.0	1.06 - 13.00	0.21 - 0.93	18.1 - 639	15	0.7162	0.2293	0.966	19
	323.0	1.06 - 13.49	0.21 - 0.93	18.1 - 656	22	0.7314	0.2294	0.964	17, 19
	333.2	2.53 - 15.90	0.36 - 0.91	44.2 - 635	11	0.8879	0.2491	0.984	17
	333.0	3.17 - 13.00	0.44 - 0.85	57.0 - 509	10	0.8022	0.1672	0.978	19
	333.0	2.53 - 15.90	0.36 - 0.91	44.2 - 635	21	0.8635	0.2236	0.979	17, 19
	343.0	1.95 - 18.29	0.26 - 0.91	32.1 - 620	10	0.9045	0.167	0.978	17

oleate	313.0	2.86 - 12.51	0.48 - 0.94	55.6 - 734	12	0.8102	0.3919	0.984	20
	313.0	2.91 - 10.77	0.42 - 0.89	56.8 - 674	4	0.9405	0.4382	0.996	16
	313.0	4.65 - 13.37	0.60 - 0.94	102 - 753	6	0.9358	0.4212	0.960	15
	313.0	2.86 - 13.37	0.42 - 0.94	55.6 - 753	22	0.8724	0.4107	0.961	15, 16, 20
	333.0	5.62 - 18.03	0.60 - 0.94	114 - 689	13	0.8738	0.281	0.967	20
	333.0	7.36 - 13.69	0.64 - 0.84	168 - 547	4	1.1303	0.3556	0.997	16
	333.0	4.05 - 18.96	0.53 - 0.92	75.8 - 707	7	0.7985	0.1632	0.954	15
	333.0	4.05 - 18.96	0.53 - 0.94	75.8 - 707	24	0.9027	0.2647	0.920	15, 16, 20
linoleate	313.0	2.86 - 11.82	0.52 - 0.94	55.7 - 715	12	0.7432	0.3574	0.978	20
	313.0	4.36 - 13.10	0.59 - 0.95	93.7 - 747	6	0.9009	0.4029	0.968	15
	313.0	2.82 - 13.10	0.52 - 0.95	55.7 - 747	18	0.7561	0.3443	0.930	15, 20
	333.0	5.62 - 18.03	0.61 - 0.95	114 - 689	14	0.8694	0.2827	0.970	20
	333.0	3.81 - 20.29	0.50 - 0.94	70.5 - 730	7	0.7888	0.1652	0.975	15
	333.0	3.81 - 20.29	0.50 - 0.95	70.5 - 730	21	0.8417	0.244	0.927	15, 20

Table 5. Parameters A^* and B^* of Eq. (3) for different CO₂ + fatty acid ethyl esters binary mixtures. R^2 : linear regression coefficient. P is given in MPa and ρ_{CO_2} in kg/m³.

fatty acid ethyl ester	T / K	P range / Mpa	X_{CO_2} range	ρ_{CO_2} range / kg·m ⁻³	N_{exp}	$-A^*$	B^*	R^2	ref.
Caproato	308.2	1.70 - 6.46	0.28 - 0.85	31.7 - 183	8	0.8923	0.4966	0.988	21
	318.2	1.70 - 7.82	0.23 - 0.85	30.4 - 229	10	0.9894	0.4472	0.985	21
	328.2	1.73 - 9.22	0.20 - 0.84	29.9 - 268	12	1.0358	0.3862	0.986	21
Caprylato	308.2	1.75 - 7.17	0.27 - 0.89	32.7 - 235	9	0.9297	0.5128	0.984	21
	318.2	1.69 - 7.82	0.24 - 0.80	30.4 - 229	10	0.9236	0.3672	0.987	21
	328.2	1.69 - 9.21	0.20 - 0.81	29.2 - 268	12	0.9907	0.3258	0.987	21
Caprato	308.2	1.66 - 7.10	0.25 - 0.84	31.0 - 229	9	0.9151	0.4528	0.979	21
	318.2	1.69 - 7.89	0.22 - 0.77	30.4 - 233	10	0.9295	0.3301	0.988	21
	328.2	1.69 - 9.21	0.20 - 0.77	29.2 - 268	11	0.9633	0.2587	0.985	21
Stearate	313.2	2.84 - 13.22	0.45 - 0.91	55.2 - 748	9	0.8011	0.3322	0.975	22
	323.2	2.70 - 15.94	0.45 - 0.90	49.6 - 721	9	0.6837	0.1702	0.981	22
	333.2	3.50 - 18.26	0.44 - 0.91	63.8 - 693	10	0.8839	0.2290	0.999	22
Oleate	313.2	2.98 - 12.50	0.52 - 0.91	58.4 - 732	9	0.7226	0.2959	0.961	22
	323.2	2.08 - 15.95	0.36 - 0.92	37.1 - 722	13	0.7311	0.2084	0.979	22
	333.2	3.14 - 18.62	0.39 - 0.96	56.3 - 700	15	0.9432	0.2580	0.993	22
Linoleate	313.2	2.00 - 12.09	0.35 - 0.94	31.7 - 721	8	0.7816	0.3455	0.986	22
	323.2	1.97 - 15.28	0.31 - 0.91	35.0 - 707	12	0.7964	0.2509	0.991	22
	333.2	2.03 - 16.97	0.29 - 0.90	34.8 - 664	13	0.8390	0.2051	0.988	22
EPA	303.1	6.00 - 11.80	0.75 - 0.90	171 - 806	5	0.5286	0.2103	0.855	23
	313.1	4.24 - 15.27	0.59 - 0.94	90.3 - 786	13	0.7339	0.2846	0.968	20
	313.1	3.04 - 14.87	0.54 - 0.92	59.8 - 779	10	0.6156	0.2048	0.971	22
	313.1	6.50 - 13.90	0.75 - 0.90	171 - 762	5	0.5628	0.1637	0.974	23
	313.1	3.04 - 15.27	0.54 - 0.94	59.8 - 786	28	0.6520	0.2291	0.961	20, 22, 23
	323.1	2.87 - 16.90	0.53 - 0.91	53.2 - 741	12	0.5627	0.1240	0.969	22

DHA	323.1	8.00 - 16.50	0.75 - 0.90	219 - 732	5	0.6238	0.1449	0.961	23
	323.1	2.87 - 16.90	0.53 - 0.91	53.2 - 741	17	0.5621	0.1203	0.967	22, 23
	333.1	2.86 - 20.79	0.28 - 0.93	50.7 - 737	14	1.0598	0.3269	0.968	20
	333.1	5.17 - 19.04	0.61 - 0.89	103 - 708	12	0.6932	0.1429	0.987	22
	333.1	9.00 - 18.90	0.75 - 0.90	235 - 705	4	0.7310	0.1617	0.996	23
	333.1	2.86 - 20.79	0.28 - 0.93	50.7 - 737	30	0.9883	0.2893	0.950	20, 22, 23
	343.1	10.20 - 21.20	0.75 - 0.90	256 - 682	5	0.7335	0.1183	0.965	23
	353.1	14.10 - 23.20	0.79 - 0.90	388 - 659	4	0.7899	0.1116	0.936	23
	313.1	4.24 - 18.03	0.53 - 0.94	90.3 - 822	13	0.7454	0.2732	0.881	20
	313.1	1.87 - 16.85	0.48 - 0.90	34.5 - 807	12	0.4432	0.1038	0.984	22
	313.1	4.70 - 17.50	0.64 - 0.95	104 - 815	6	0.6181	0.1917	0.992	23
	313.1	1.87 - 18.03	0.48 - 0.95	34.5 - 822	31	0.5126	0.1415	0.892	20, 22, 23
	323.1	2.29 - 17.38	0.55 - 0.89	41.2 - 766	12	0.3850	0.0174	0.966	22
	323.1	5.50 - 20.00	0.64 - 0.95	119 - 785	7	0.6906	0.1745	0.993	23
	323.1	2.29 - 20.00	0.55 - 0.95	41.2 - 785	19	0.4317	0.0472	0.920	22, 23
	333.1	7.00 - 23.54	0.67 - 0.94	156 - 772	13	0.6659	0.1283	0.977	20
	333.1	2.79 - 19.22	0.48 - 0.88	49.3 - 711	8	0.5746	0.0688	0.993	22
	333.1	2.79 - 23.54	0.48 - 0.94	49.3 - 772	21	0.6038	0.0949	0.984	20, 22

Table 6. Pure component parameters employed in the GC-EoS calculations.

	T_c / K	P_c / MPa	d_c cm·mol ⁻¹	Ref. for T_c and P_c values
hexadecane	720.6	1.42	7.174	10
eicosane	768.0	1.16	8.072	10
decanol	687.0	2.22	5.995	12
hexadecanol	724.2	1.57	7.186	13
oleic acid	781.0	1.37	8.056	26
methylmyristate	707.9	14.2	7.273	26
methyloleate	767.0	10.5	7.969	26
ethyloleate	784.2	1.05	8.049	26

Table 7. Comparison between the average absolute deviations (*AAD*%) obtained in the calculation of CO₂ solubility (mole fractions) in liquid high-molecular weight substances using the density-dependent correlation (Eq. 3) and the GC-EoS model.

	GC-EoS correlation	Eq. (3) correlation	Ref. for experimental data
hexadecane	6.96	2.30	8, 9
eicosane	1.98	2.73	10
decanol	9.63	4.63	12
hexadecanol	14.66	5.65	13
oleic acid	1.97	2.06	14
methylmyristate	11.12	6.16	17, 19
methyloleate	4.22	3.71	15,16, 20
ethyloleate	2.94	2.30	22

FIGURE CAPTIONS

FIGURE 1. Linear correlation between $\ln(X_{CO_2})$ and $\ln(\rho_{CO_2})/P$ (Eq. 3) for binary mixtures of CO_2 with high molecular weight alkanes. (■) n-hexadecane⁸, 323.15 K; (▲) eicosane¹⁰, 339.1 K; (●) tetracosane¹¹, 423.2 K.

FIGURE 2. Linear correlation between $\ln(X_{CO_2})$ and $\ln(\rho_{CO_2})/P$ (Eq. 3) for binary mixtures of CO_2 with fatty acid methyl esters. (■) methyl palmitate¹⁷, 323.15 K; (▲) methyl laureate¹⁸, 323 K; (○) methyl oleate²⁰, 333 K; (×) methyl linoleate¹⁵, 333 K.

FIGURE 3. Solubility of $SCCO_2$ in oleic acid at 313 K. (a) Comparison between the data reported by different authors: (●) Zou et al.¹⁵; (▲) Bharath et al.¹⁴; (◆) Yu et al.¹⁶. (b) Linear correlation between $\ln(X_{CO_2})$ and $\ln(\rho_{CO_2})/P$ (Eq. 3) obtained considering separately each source of experimental data.

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FIGURE 3. Solubility of SCCO₂ in oleic acid at 313 K. (a) Comparison between the data reported by different authors: (●) Zou et al.¹⁵; (▲) Bharath et al.¹⁴; (◆) Yu et al.¹⁶. (b) Linear correlation between $\ln(X_{CO_2})$ and $\ln(\rho_{CO_2})/P$ (Eq. 3) obtained considering separately each source of experimental data.