

A New Method for Estimating Solubility of Fatty Acids, Esters, and Triglycerides in Supercritical Carbon Dioxide

Vanessa R. Vasconcellos and Fernando A. Cabral*

Department of Food Engineering, DEA-FEA, State University of Campinas–UNICAMP, Campinas, SP, Brazil, 13083-970

ABSTRACT: A method to predict solubility of fat compounds (fatty acids, fatty acid esters, and triglycerides) in supercritical CO₂ in the absence of experimental data is presented. The method is based on the idea of group contribution, so only knowledge about the chemical structure of the substance is needed to predict its solubility in CO₂. Chrastil's equation was used to correlate the solubilities of fatty acids, fatty acid esters, and triglycerides in CO₂. The three parameters determined from fitting of the data were calculated. A nonlinear fit routine was used to determine the chemical group contributions to the three parameters. Analysis of the results shows that it is possible to correlate the parameters of Chrastil's equation to molecular groups. The average deviation from the experimental data was 8%.

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KEY WORDS: Chrastil equation, fatty acid esters, fatty acids, group contribution method, prediction of solubility, supercritical carbon dioxide.

Supercritical solvents exhibit properties intermediate between gases and liquids. They exhibit viscosities and diffusivities comparable to those of gases, yet densities comparable to liquids. Consequently, mass transfer rates may approach those of gases and solubilities those of liquids

Review of literature on edible oils points to strong interest in purification and fractionation processes involving near-critical and supercritical fluids. Potential applications range from extraction of vegetable oils from various crops such as soybeans and canola to fractionation of alkyl esters derived from fish oils, resulting in concentration of individual ω-3 fatty acids.

To evaluate applications for supercritical extraction and fractionation, one must be able to estimate the solubility of the material in the supercritical solvent. One way to do this is using the model developed by Chrastil (1), which correlates solubility as a function of temperature and density, by adjusting three parameters to the experimental data. The Chrastil equation has been used to correlate experimental data of different substances in supercritical gases, especially for modeling solubility of oils and its components.

Since the experimental approach to supercritical fluid extraction is understandably complex, time-consuming, and very expensive, it is of paramount importance to have theoretical methods that can be used to evaluate the solubility of a solute and how it varies with pressure and temperature of a fluid in the supercritical range (2).

In this paper, a group contribution method is developed to allow the estimation of the three parameters of the Chrastil equation and in this way predict solubility of fatty acids, fatty acid esters, and triglycerides in supercritical carbon dioxide (SC-CO₂) in the absence of experimental data, based uniquely upon the chemical structure.

MATERIALS AND METHODS

Experimental solubility data were collected from literature (1,3–18) for the following systems: lauric acid (C12), myristic acid (C14), palmitic acid (C16), stearic acid (C18), oleic acid (C18:1), linoleic acid (C18:2), methyl myristate (mC14), methyl palmitate (mC16), methyl stearate (mC18), methyl oleate (mC18:1), ethyl stearate (eC18), ethyl oleate (eC18:1), ethyl linoleate (eC18:2), ethyl eicosapentanoate (EPA), ethyl docosahexanoate (DHA), triolein (OOO), tristearin (SSS), tripalmitin (PPP), and trilinolein (LLL). All the experimental data were written in terms of the mass fraction Y (kg solute/kg CO₂). The concentration of the solute in the light phase is low, so it is possible to consider the density of the light phase as being equal to the CO₂ density at the same temperature and pressure conditions, which was calculated with the Huang equation (19) and which reproduces experimental values from Angus *et al.* (20).

Chrastil's equation was used to correlate the experimental data. Chrastil assumed formation of a solvato complex between solute and solvent molecules (in this case, CO₂ molecules) in the dense gas phase. At phase equilibrium, Chrastil's model gives a linear relationship between the logarithm of solubility and the logarithm of SC-CO₂ density [Maheshwari *et al.* (3)], which can be expressed in Equation 1:

$$\ln Y = (k - 1) \ln \rho + \left(\frac{a}{T} + b \right) \quad [1]$$

where Y is the solubility (kg/kg CO₂), ρ is the density of the SC-CO₂ (kg/m³), and T is the temperature (K). The constants

*To whom correspondence should be addressed at Department of Food Engineering, DEA-FEA, State University of Campinas–UNICAMP, P.O. Box 6121, Campinas, SP, Brazil, 13083-970.
E-mail: cabral@ceres.fea.unicamp.br

TABLE 1
Group Contributions Values^a

Groups	Δk	Δa	Δb
P_0	14.863	-676.93	-85.967
CH_3-	-0.5000	-180.00	3.4450
$-\text{CH}_2-$	-0.5000	-180.00	3.4450
$-\text{HC}=\text{CH}-$	1.5132	-1600.0	-5.743
$-\text{COOH}$	0.165	-3254.9	6.7829
$-\text{COOCH}_3$	-0.7295	1551.9	1.4028
$-\text{COOCH}_2\text{CH}_3$	-1.5577	2097.9	5.0816
Glycerate (Fig. 1) for unsaturated substances	4.8774	10507	-49.299
Glycerate (Fig. 1) for saturated substances.	21.887	1625.9	-140.55

^a Δk , Δa , Δb group contribution to the parameters k , a , b , respectively.

k , a , and b are parameters to be adjusted to the experimental data by linear regression analysis.

The three parameters of the Chrastil equation were obtained for the systems: C12, C14, C16, C18:1, C18:2, mC14, mC16, mC18, mC18:1, eC18:1, eC18:2, SSS, and OOO [this last one from Ribeiro and Bernardo-Gil (4)].

These values were used to determine the group contributions in the simple model in Equation 2:

$$q(i) = P_0 + \sum_{j=1}^{NG} (\Delta q)_j \quad [2]$$

where q is the parameter k , a , or b for the molecule i ; P_0 is a constant determined separately for each parameter; and $(\Delta q)_j$ is the group contribution (Δk , Δa , or Δb) for the parameter q . A nonlinear fit routine (Simplex method, using the program package Statistica; Statsoft, Tulsa, OK) was used to determine these group contributions, which are listed in Table 1. For triglycerides, it was defined as a group called Glycerate, represented in Figure 1.

Once the three parameters were estimated through group contribution, they were substituted in the Chrastil's equation, and the solubility Y_{calc} was calculated. The deviations were

$$X_j = \frac{Y_{\text{exp}} - Y_{\text{calc}}}{Y_{\text{exp}}} \quad [3]$$

$$X_m = \frac{1}{\text{NED}} \sum_{j=1}^{\text{NED}} X_j \quad [4]$$

obtained using the relations Equations 3–5:

$$E_m = \frac{1}{\text{NED}} \sum_{j=1}^{\text{NED}} |X_j| \quad [5]$$

where NED is the number of experimental data points; Y_{calc} and Y_{exp} are the calculated and experimental solubility values, respectively, and $|X_j|$ is the module of X_j .

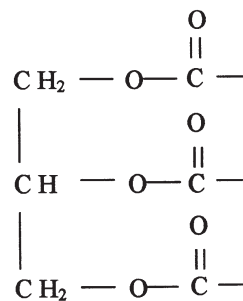


FIG. 1. The glycerate group.

RESULTS AND DISCUSSION

For all the substances studied, the experimental data published by different investigators presented great discrepancies, as illustrated in Figure 2 for oleic acid. Figure 2 also shows the predicted values for this substance, using group contribution. Different authors from the literature were selected for each substance in order to maintain a greater universe of data. It is reasonable to suppose that the correct value must be in this range of data. This choice leads to greater X_m and E_m values, because there is only one calculated solubility value for a given pressure and temperature, but different—sometimes very different—experimental solubility values.

Table 2 shows the parameters k , a , and b obtained by group contribution as well as the deviations between the calculated solubility values and the experimental ones. The deviations X_m and E_m seem to be quite high, but it must be stressed that they are a mean over the deviations calculated with different experimental data, from different authors, compared to different values of data.

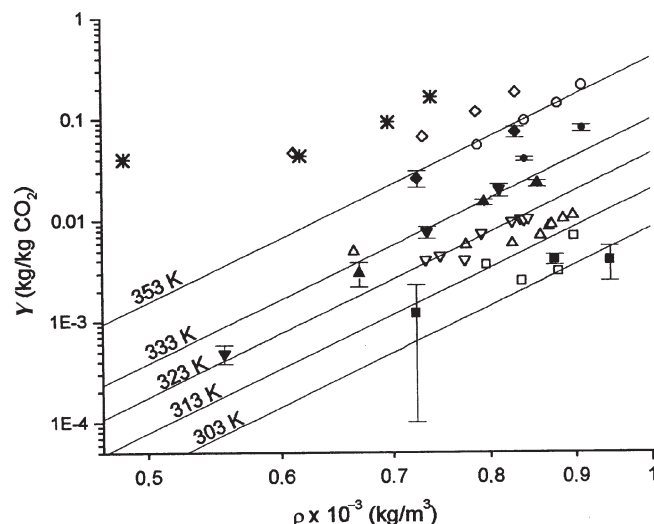


FIG. 2. Comparison between experimental data published by different authors for a CO_2 -oleic acid (C18:1) system. The lines are the predicted solubilities using the Chrastil's equation with the parameters estimated by group contribution. Following are the temperatures and references: \square 303 K (15); \blacksquare 313 K (3); \circ 313 K (8); \bullet 313 K (10); \blacktriangle 313 K (15); \triangle 323 K (3); ∇ 323 K (15); \blacktriangledown 333 K (3); \diamond 333 K (8); \blacklozenge 333 K (10); $*$ 353 K (8). Error bars were defined by cited authors.

TABLE 2
Parameters k , a , and b Estimated by Group Contributions and Deviations Between the Predicted and Experimental Solubility Values^a

System	k	a	b	X_m (%)	E_m (%)
C12	9.53	-5912	-41.3	-8.9	26
C14	8.53	-6272	-33.9	11	43
C16	7.53	-6632	-27.5	14	46
C18:1	9.02	-8232	-32.8	-39	53
C18:2	11.6	-9472	-45.5	19	26
mC14	7.63	-1425	-39.8	37	37
mC16	6.63	-1825	-32.8	13	28
eC18	4.81	-1639	-22.3	47	48
mC18:1	8.10	-3425	-38.6	4.1	27
eC18:1	7.32	-2879	-35.0	5.3	17
eC18:2	9.83	-4119	-47.6	-7.8	19
OOO	1.78	-3070	2.529	—	—
SSS	9.75	-8771	-39.4	-11	12
C18*	5.53	-6992	-21.5	0.90	58
mC18*	5.63	-2185	-26.0	18	33
EPA (eC20:5)*	16.4	-8199	-78.6	46	51
DHA (eC22:6)*	17.9	-9799	-84.3	-47	52
PPP*	12.8	-7691	-60.5	3.5	37
LLL*	9.32	-6790	-35.4	80	142

^aAsterisk (*) indicates substances that did not participate in the fit routine to determine the group contributions k , a , b parameters of the Chrastil's equation estimated by group contribution, X_m , E_m deviation, Equations 3 to 5. OOO, triolein; SSS, tristearin; PPP, tripalmitin; LLL, trilinolein; EPA, ethyl eicosapentanoate; DHA, ethyl docosahexanoate; C12, lauric acid; C14, myristic acid; C16, palmitic acid; C18, stearic acid; C18:1, oleic acid; C18:2, linoleic acid; C14, methyl myristate; C16, methyl palmitate; eC18, ethyl stearate; C18, methyl oleate; eC18:1, ethyl oleate; eC18:2, ethyl linoleate; C18, methyl stearate.

For triglycerides, the quantity of experimental data found in literature was not sufficient to make a more consistent statistical analysis; so, it was only possible to adjust a model by considering two different values for the "glycerate" group, one for saturated and the other for unsaturated substances.

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