Solubility of β-Carotene in Near-Critical Mixtures of (Ethane + Propane)

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The solubility of synthetic *trans*-β-carotene was measured in two near-critical solvent mixtures of (ethane + propane) (mixtures I and II containing 50 mol % and 60 mol % propane, respectively) using a flow apparatus. The measurements were carried out at the temperatures (333.15, 343.15, and 348.15) K for solvent mixture I and at (313.15, 333.15, and 343.15) K for mixture II, at pressures ranging from (5.0 to 30.0) MPa. The solubility measurements were correlated with the Chrastil equation.

Introduction

β-Carotene is a hydrocarbon ($C_{40}H_{56}$) having a highly unsaturated chain forming a chromophore responsible for its yellow-orange color. The compound is used as a coloring agent in the food industry, and its pro-vitamin A and antioxidant properties are also well established.[1]

In the past two decades supercritical fluid technology has received considerable attention as a viable alternative and promising new technique for separation and recovery of highly nonvolatile organic compounds.[2] Solubility studies of β-carotene in carbon dioxide and other supercritical solvents have appeared in the literature,[3−13] but the bulk of these studies dealt mainly with single-solvent systems. However, the use of solvent mixtures can simultaneously increase the solvent power and maintain the operation temperature of supercritical systems below the value at which degradation of the compound occurs. For instance, propane has a critical temperature of 369.85 K, but β-carotene, which is sensitive to heat, can suffer degradation[10] at such temperature. However, an ethane and propane mixture has a lower critical temperature, since the critical temperature for ethane is 305.35 K.

On the other hand, theoretical studies for the calculation of the solubilities of benzoic acid and phenanthrene in mixtures of carbon dioxide and propane showed that the solubility of these compounds was about 100 times higher than that in pure carbon dioxide.[14]

The objective of the present work, following our previous determination of the solubility of β-carotene in supercritical carbon dioxide and in supercritical ethane,[11] was to measure the solubility of the same compound in near-critical mixtures of ethane and propane, compare the results with those obtained with single solvents, and correlate them with an appropriate equation.

Experimental Section

Synthetic *trans*-β-carotene (type 1, 95% purity) was purchased from Sigma. Solvent mixture I, containing ethane and propane (99.995% purity) with 50 mol % propane, was obtained from Praxair (Portugal). Solvent mixture II, containing ethane and propane (99.995% purity) with 60 mol % propane, was obtained from Air Liquide (Portugal). Both cylinders, with a volume of 50 L, were filled with the gases to give the overall composition indicated and were provided with full-length eductor tubes for liquid withdrawal. The hexane (p.a) was purchased from Merck.

Before the solubility measurements, the synthetic *trans*-β-carotene was submitted to supercritical CO_2 (typically 150 g of CO_2 per g of compound) in order to remove impurities interfering in spectrophotometric analysis.[11]

The flow type apparatus (Figure 1) used in these studies was described in detail in a previous paper.[15] It was tested through solubility measurements of naphthalene in supercritical carbon dioxide, and recently it was also used to carry out the determination of the solubility of β-carotene in supercritical carbon dioxide and ethane.[11]

With reference to Figure 1, the liquid solvent mixture was pumped from the cylinder, 1, to the equilibrium cell, 11, through a positive-displacement minipump, 5, with the pressure controlled by a back-pressure regulator, 8. The equilibrium cell, a 32 cm^3 vessel filled with 8 g of synthetic *trans*-β-carotene mixed with glass beads and enclosed between two layers of glass wool, was immersed in a controlled temperature water bath, 16. The temperature of the bath was measured with a platinum resistance thermometer, with the uncertainty ±0.1 K. The pressure inside the cell was measured with a Bourdon type Heise gauge, 7, with the uncertainty ±0.05 MPa.

The near-critical solvent mixture was expanded to atmospheric pressure through a three-way valve, 12, heated to the temperature of the bath, and the solute was collected in a cooled glass U-tube, 13, filled with glass wool. The gas flow rate was monitored through a rotameter, 14, and the total volume was measured with a wet test meter, 15, with the uncertainty ±0.005 L. The actual compositions of the mixtures of propane and ethane were checked by GC, and they agreed with the overall compositions of the cylinders.

At the end of each run, the inside of the three-way valve and expanding tubing, as well as the glass wool inside the U-tube, was washed with hexane, to recover all the β-carotene. The hexane contained 0.2 wt % of an antioxidant, 2,6-di-*tert*-butyl-4-methylphenol, to avoid the degradation of the solute.[16,17] The presence of the antioxidant did not interfere with the spectrophotometric analysis.

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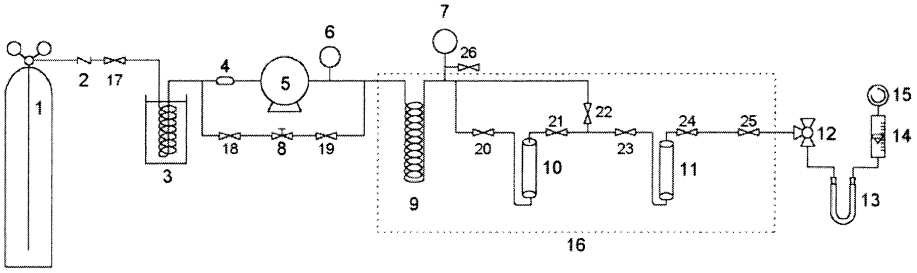

Figure 1. Schematic diagram of the apparatus for measurements of the solubility of *trans*-β-carotene in supercritical solvent mixtures: 1, cylinder; 2, check valve; 3, ice cooler; 4, filter; 5, pump; 6 and 7, manometers; 8, back-pressure regulator; 9, heat exchanger; 10, high-pressure cell; 11, equilibrium cell; 12, three-way valve; 13, glass U-tube; 14, rotameter; 15, wet test meter; 16, water bath; 17−26, valves.

Before each solubility measurement, the system was purged, removing 10 L of expanded gas, to ensure the saturation of the lines following the equilibrium cell. The system was then allowed to equilibrate for 1 h, after which the solubility was measured by passing about 5 L of gas (STP) at a low flow rate (0.1 L/min, STP).

The amount of the collected *trans*-β-carotene, in known volumes of hexane, was determined by UV−visible spectrophotometry (Spectrophotometer Hitachi U-2000), using the Lambert−Beer law, $A = abc$, in which A is the absorbance, a is the absorptivity, b is the light path, and c is the concentration of the compound in hexane.

UV−visible spectra were run, between (300 and 500) nm, and the absorbance was measured, with an uncertainty of ±0.002, at 450 nm (wavelength of the maximum absorbance of *trans*-β-carotene in hexane). A value of 259.2 L/(g·cm) was used for the absorptivity of β-carotene[18] in hexane at 450 nm. The spectrophotometer was checked regularly with standard solutions of known concentration of synthetic *trans*-β-carotene.

Results and Discussion

The solubility of *trans*-β-carotene in near-critical solvent mixtures of ethane and propane was determined at the temperatures (313.15, 333.15, 343.15, and 348.15) K and at pressures up to about 30.0 MPa. The results are an arithmetic average of two to four measurements. For the near-critical solvent mixture of ethane and propane containing 50 mol % propane (mixture I), the reproducibility of the solubility measurements was within 11% at pressures below 10 MPa, while, for the near-critical solvent mixture of ethane and propane containing 60 mol % propane (mixture II), the reproducibility was 9%. At pressures above 10 MPa, the reproducibility was within 5% for both mixtures. The obtained mole fractions for *trans*-β-carotene ranged from 3.7×10^{-7} to 9.4×10^{-5}, at 5.1 MPa (348.15 K) and 30.1 MPa (348.15 K), respectively, for mixture I, and from 5.1×10^{-6} to 9.2×10^{-5}, at 5.1 MPa (343.15 K) and 30.1 MPa (343.15 K), respectively, for mixture II. The average experimental error was ±4%, for mixture I, and ±3%, for mixture II.

Tables 1 and 2 show the solubility (in both mole fraction and mass of solute per volume unit of near-critical fluid) of *trans*-β-carotene in the two mixtures of ethane and propane. These results are plotted as a function of pressure in Figures 2 and 3.

The solubility of *trans*-β-carotene increases in both near-critical solvent mixtures with pressure at constant temperature. The crossover pressure (the solubility above this value increases with the temperature) is between (7.0 and 9.0) MPa, for mixture I, and around 5.0 MPa for mixture II. With pure supercritical ethane, the crossover pressure of the solubility of β-carotene was between (11.5 and 12.5) MPa.[11] The trend seems to indicate a decrease of the value of this pressure as the amount of propane increases.

Table 1. Solubility of *trans*-β-Carotene in a Near-Critical Mixture of Ethane and Propane Containing 50 mol % Propane (Mixture I)

T	P	ρ		10^3S	P	ρ		10^3S
K	MPa	g·dm^{-3}	10^6x	g·dm^{-3}	MPa	g·dm^{-3}	10^6x	g·dm^{-3}
333.15	5.1	355.1	3.0	14.9	17.6	436.3	22.4	136.6
	7.1	381.1	6.2	33.0	20.1	444.1	26.4	163.8
	9.1	397.1	7.8	43.3	25.1	457.4	35.9	229.4
	15.1	427.3	19.3	115.0	30.1	468.4	43.8	286.6
343.15	5.1	283.3	1.2	4.9	17.6	421.7	34.2	201.2
	7.1	350.1	7.0	34.4	20.1	430.6	45.9	275.6
	9.1	373.6	11.6	60.7	25.1	445.4	60.8	378.0
	11.6	392.6	14.8	81.3	30.1	457.4	73.2	467.2
	15.1	411.3	25.3	145.5				
348.15	5.1	169.1	0.4	0.8	17.6	414.2	43.9	253.9
	7.1	331.0	3.9	18.1	20.1	423.7	63.0	372.6
	9.1	360.6	8.4	42.0	25.1	439.3	77.7	476.3
	11.6	382.4	24.2	129.3	30.1	452.0	93.7	590.9
	15.1	403.0	35.8	201.5				

Table 2. Solubility of *trans*-β-Carotene in a Near-Critical Mixture of Ethane and Propane, Containing 60 mol % Propane (Mixture II)

T	P	ρ		10^2S	P	ρ		10^2S
K	MPa	g·dm^{-3}	10^6x	g·dm^{-3}	MPa	g·dm^{-3}	10^6x	g·dm^{-3}
313.15	5.1	432.4	5.6	3.2	17.6	475.1	10.3	6.6
	7.1	442.0	5.2	3.1	20.1	480.8	13.7	8.9
	9.1	450.0	5.4	3.3	30.1	499.5	19.9	13.4
	15.1	468.8	9.4	5.9				
333.15	5.1	381.3	5.8	3.0	17.6	448.3	31.1	18.8
	7.1	400.1	9.3	5.0	20.1	455.7	36.9	22.7
	9.1	413.4	15.8	8.9	30.1	478.5	65.4	42.2
	15.1	440.1	29.5	17.6				
343.15	5.1	341.1	5.1	2.4	15.1	424.8	38.4	22.0
	7.1	373.8	10.4	5.2	17.6	434.3	52.6	30.8
	9.1	392.0	19.1	10.1	20.1	442.6	59.8	35.8
	11.6	408.1	28.7	15.8	30.1	467.8	92.3	58.2

In Figure 4 is presented the comparison of the solubility of *trans*-β-carotene obtained in this work at 333.15 K with our published data of the solubility of the same compound in ethane[11] at the same temperature and in liquid propane at 288.15 K.[9] The solubility of *trans*-β-carotene at 333.15 K in mixture II was about 2 orders of magnitude higher than that in ethane at low pressures, 1 order of magnitude higher than in that ethane at high pressures, and almost two times higher than that in mixture I. The solubility of *trans*-β-carotene for pressures higher than 10 MPa, for both mixtures, is also higher than the value reported in the literature[9] for the solubility of the same compound in liquid propane.

The increasing solubility of *trans*-β-carotene with the amount of propane in the mixture can be explained by the

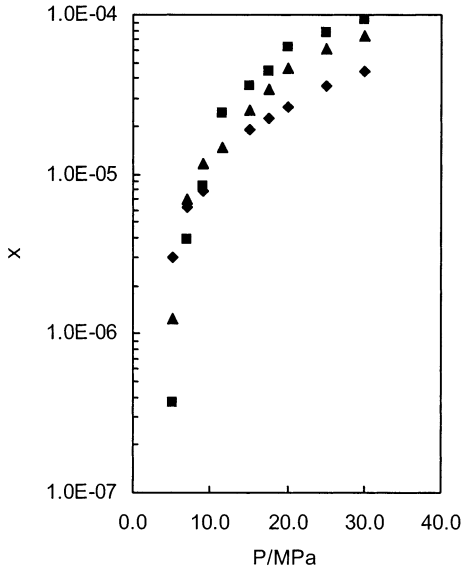

Figure 2. Mole fraction solubility x of *trans*-β-carotene in a near-critical mixture of ethane and propane, containing 50 mol % propane (mixture I), as a function of pressure: ◆, 333.15 K; ▲, 343.15 K; ■, 348.15 K.

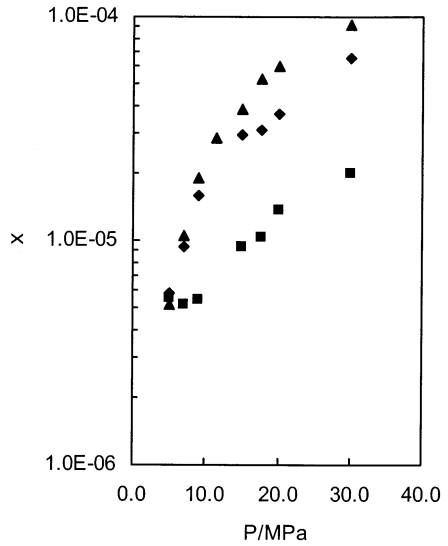

Figure 3. Mole fraction solubility x of *trans*-β-carotene in a near-critical mixture of ethane and propane, containing 60 mol % propane (mixture II), as a function of pressure: ■, 313.15 K; ◆, 333.15 K; ▲, 343.15 K.

fact that propane is a better solvent for *trans*-β-carotene than ethane, because, although both fluids are nonpolar, propane has a higher polarizability[9] than ethane (6.3×10^{-24} cm^3 and 4.4×10^{-24} cm^3, respectively).

Correlation of the Solubility Results

The Chrastil[19] equation was used to correlate the solubility of β-carotene in near-critical mixtures of ethane and propane. Although cubic equations of state can be more reliable for the estimation of the solubility of solid compounds in supercritical fluids, their applicability requires the knowledge of solute critical parameters, which are not possible to determine experimentally, since compounds such as β-carotene undergo degradation at such high temperatures. However, these parameters can be predicted with correlations. With the Chrastil correlation, its estimated parameters have an easily identifiable physical meaning.[19−21]

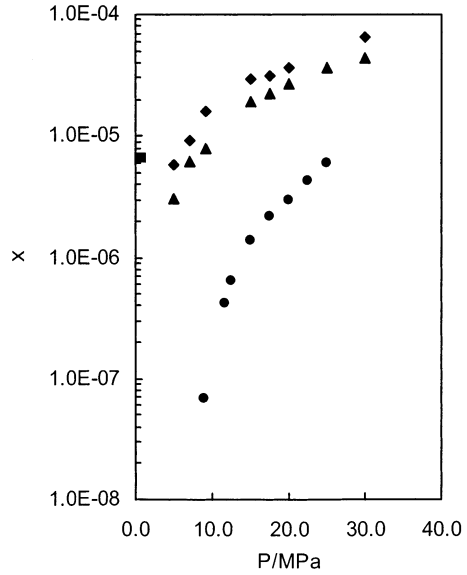

Figure 4. Mole fraction solubility x of *trans*-β-carotene as a function of pressure: ▲, 333.15 K, near-critical mixture of ethane and propane containing 50 mol % propane (mixture I); ◆, 333.15 K, near-critical mixture of ethane and propane containing 60 mol % propane (mixture II); ●, 333.15 K, ethane;[11] ■, 288.15 K, propane.[9]

This model postulates that the association between solvent and solute molecules results in formation of a solvated complex. In an ideal case, k molecules of solvent A associate with one molecule of solute B to form a solvated complex BA_k. The association constant k is characteristic for a given solvent and solute system. From equilibrium considerations and entering with the Clausius−Clapeyron equation, the following correlation was derived:[19]

$$\ln(S) = k \ln(\rho) + \frac{a}{T} + b \tag{1}$$

in which

$$a = \frac{\Delta_r H}{R} \tag{2}$$

$$b = \ln\left(\frac{M_A + kM_B}{M_B{}^k}\right) + q \tag{3}$$

and where S is the solubility of the solute, ρ is the density of the solvent, k is the number of molecules of the solvent associated with one molecule of solute, $\Delta_r H$ is the total reaction enthalpy (sum of the enthalpy of vaporization of the solute and the enthalphy of solvation), q is a constant, M_A is the molar mass of the solute, and M_B is the molar mass of the solvent.

The densities for the near-critical mixtures of ethane and propane were obtained with the program NIST-NSB[22] and are listed in Tables 1 and 2. The parameters of the Chrastil equation for the two solvent mixtures and for pure ethane[23] are presented in Table 3. For each mixture of solvents, the values of k were similar for the several isotherms, so the average value was considered and introduced in eq 1, allowing that the lines be parallel, as predicted by the model. The term $a/T + b$ was represented as a linear function of $1/T$, allowing the determination of a and b. Figures 5 and 6 show the best fit of eq 1 to the experimental data, for mixtures I and II, respectively. The comparison between the calculated and experimental results shows

Table 3. Parameters of the Chrastil Equation for the Calculation of the Solubility of *trans*-β-Carotene in the Two Near-Critical Mixtures of Ethane and Propane and in Pure Ethane

gas mixture/ propane mol %	k	a	b	AARD %[a]
60	10.94	−8260.3	−43.63	8.85
50	10.64	−8918.8	−39.92	9.84
0[23]	12.98	−7555.3	−52.97	7.00

[a] AARD $= 1/n\sum_{i=1}^{n} |s_i^{exp} - s_i^{cal}|/s_i^{exp}$ (eq 4), where the superscript "cal" denotes calculated solubility and the superscript "exp" denotes experimental solubility.

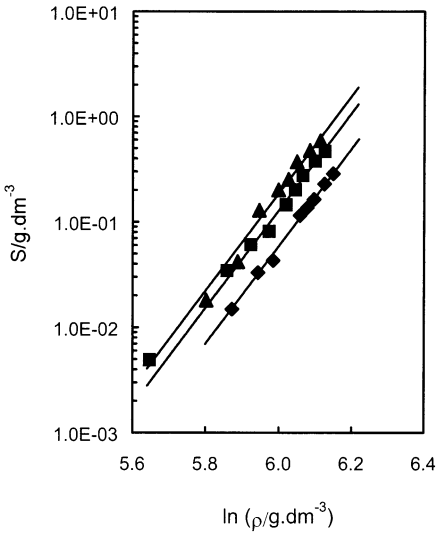

Figure 5. Solubility S of *trans*-β-carotene as a function of ln ρ, where ρ is the solvent density, in a near-critical mixture of ethane and propane containing 50 mol % propane (mixture I): ◆, 333.15 K; ■, 343.15 K; ▲, 348.15 K; —, eq 1.

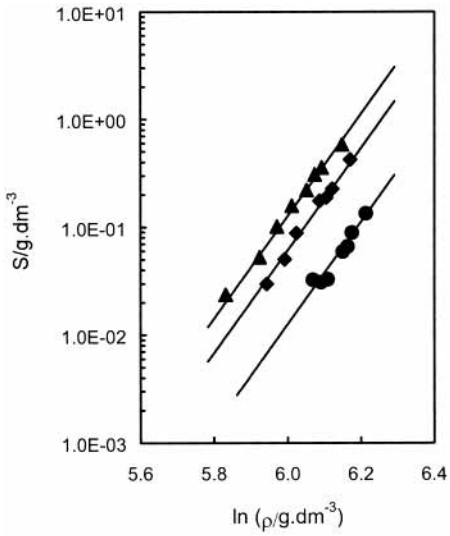

Figure 6. Solubility S of *trans*-β-carotene as a function of ln ρ, where ρ is the solvent density, in a near-critical mixture of ethane and propane containing 60 mol % propane (mixture II): ●, 313.15 K; ◆, 333.15 K; ▲, 343.15 K; —, eq 1.

average absolute relative deviations, AARDs (eq 4), of 10% for mixture I and 9% for mixture II.

The association numbers in the Chrastil equation, parameter k, are very similar for both mixtures of solvents and lower than the value obtained with supercritical ethane.[23] This shows a higher solubility dependence on solvent density for *trans*-β-carotene in supercritical ethane than in the mixtures of ethane and propane.

Conclusions

Solubilities of *trans*-β-carotene in near-critical solvent mixtures of propane and ethane were determined, and it was verified that their values were higher than those in pure ethane. Moreover, the solubility increased with the amount of propane in the mixture.

When the natural logarithm of solubility was plotted against the natural logarithm of density, a linear correlation was obtained and the isotherms were maintained parallel, as predicted by the Chrastil equation.

The slope (k) of the solubility isotherms was about the same for both solvent mixtures. However, this value was lower than that obtained with pure ethane.

Literature Cited

(1) Mordi, R. C. Carotenoids: functions and degradation. *Chem. Ind.* **1993**, 79−83.

(2) Brunner, G. *Gas Extraction*; Springer: New York, 1994.

(3) Cygnarowicz, M. L.; Maxwell, R. J.; Seider, W. D. Equilibrium Solubilities of β-carotene in Supercritical Carbon Dioxide. *Fluid Phase Equilib.* **1990**, *59*, 57−71.

(4) Chang, C. J.; Randoph, A. D. Precipitation of Microsize Organic Particles from Supercritical Fluids. *AIChE J.* **1989**, *35*, 1876−1882.

(5) Sakaki, K. Solubility of β-carotene in Dense Carbon Dioxide and Nitrous Oxide from 308 to 323K and from 9.6 to 30 MPa. *J. Chem. Eng. Data* **1992**, *37*, 249−251.

(6) Subra, P.; Sandrine, C.; Ksibi, H.; Garrabos, Y. Contribution to the Determination of the Solubility of β-carotene in Supercritical Carbon Dioxide and Nitrous Oxide: experimental data and modeling. *Fluid Phase Equilib.* **1997**, *131*, 269−286.

(7) Johannsen, M.; Brunner, G. Solubilities of the Fat-soluble vitamins A, D, E and K in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1997**, *42*, 106−111.

(8) Skerget, M.; Kzen, Z.; Habulin, M. Solubility of β-carotene and Oleic Acid in Dense CO_2 and Data Correlation by a Density Based Model. *Fluid Phase Equilib.* **1995**, *109*, 131−138.

(9) Jay, A. J.; Steytler, D. C. Near Critical Fluids as Solvents for β-carotene. *J. Supercrit. Fluids* **1992**, *5*, 274−282.

(10) Tuma, D.; Schneider, G. M. Determination of the Solubilities of Dyestuffs in Near- and Supercritical Fluids by a Static Method up to 180 MPa. *Fluid Phase Equilib.* **1999**, *158−160*, 743−757.

(11) Mendes, R. L.; Nobre, B. P.; Coelho, J. P.; Palavra, A. F. Solubility of β-carotene in Supercritical Carbon dioxide and Ethane. *J. Supercrit. Fluids* **1999**, *16*, 99−106.

(12) Sovová, H.; Stateva, R. P.; Galushko, A. A. Solubility of β-carotene in supercritical CO2 and the effect of entrainers. *J. Supercrit. Fluids* **2001**, *21*, 195−203.

(13) Hansen, B. N.; Harvey, A. H.; Coelho, J. A. P.; Palavra, A. M. F.; Bruno, T. J. Solubility of Capsaicin and β-carotene in Supercritical Carbon Dioxide and in Halocarbons. *J. Chem. Eng. Data* **2001**, *46*, 1054−1058.

(14) Joshi, D. K.; Prausnitz, J. M. Supercritical Fluid Extraction with Mixed Solvents. *AIChE J.* **1984**, *30*, 522−525.

(15) Mendes, R. L.; Coelho, J. P.; Fernandes, H. M.; Marrucho, I. J.; Cabral, J. M. S.; Novais, J. M.; Palavra, A. F. Applications of Supercritical Fluid Extraction to Microalgae and Plants. *J. Chem. Technol. Biotechnol.* **1995**, *62*, 53−59.

(16) Mendes, R. L.; Fernandes, H. L.; Roxo, C. H.; Novais, J. M.; Palavra, A. F. Solubility of Synthetic and Natural β-carotene in Supercritical Carbon Dioxide. *Proceedings of the Fourth Italian Conference on Supercritical Fluids and their Applications*, Capri (Italy), 1997; pp 423−430.

(17) Cocero, M. J.; González, S.; Pérez, S.; Alonso, E. Supercritical Extraction of Unsaturated Products. Degradation of β-carotene in Supercritical Extraction Processes. *J. Supercrit. Fluids* **2000**, *19*, 39−44.

(18) Rowan, K. S. *Photosynthetic Pigment of Algae*; Cambridge University Press: Cambridge, 1989.

(19) Chrastil, J. Solubility of Solids and Liquids in Supercritical Gases. *J. Phys. Chem.* **1982**, *86*, 3016−3021.

(20) Gurdial, G. S.; Wells, P. A.; Foster, N. R.; Chaplin, R. P. The Role of Polarity in Correlations of Solid-supercrtical Fluid Phase Systems. *J. Supercrit. Fluids* **1989**, *2*, 85−96.

(21) Ponte, M. N.; Menduiña, C.; Pereira, P. J. Solubilities of Tocopherols in Supercritical CO_2 Correlated by the Chrastil Equation, The 4th International Symposium on Supercritical fluids, Sendai (Japan), 1997; Tohoku University Press: Sendai, Japan, pp 303−305.
(22) NBS Standard Reference Database 14−DDMIX−Mixture Program Properties, National Institute of Standards and Technology: Gaithersburg, MD, 1989.
(23) Nobre, B. P.; Palavra, A. F.; Mendes, R. L. Correlation of the Solubility of β-carotene in Supercritical Carbon Dioxide and Ethane with Chrastil and Reid Equations. Fifth Conference on Supercritical Fluids and their Applications, Garda (Italy), 1999; University of Padova: Padova, Italy, pp 595−601.

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