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HSP50

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Application of the Hansen solubility theory for the selection of co-solvents for supercritical carbon dioxide extraction

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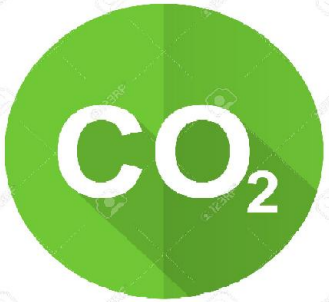
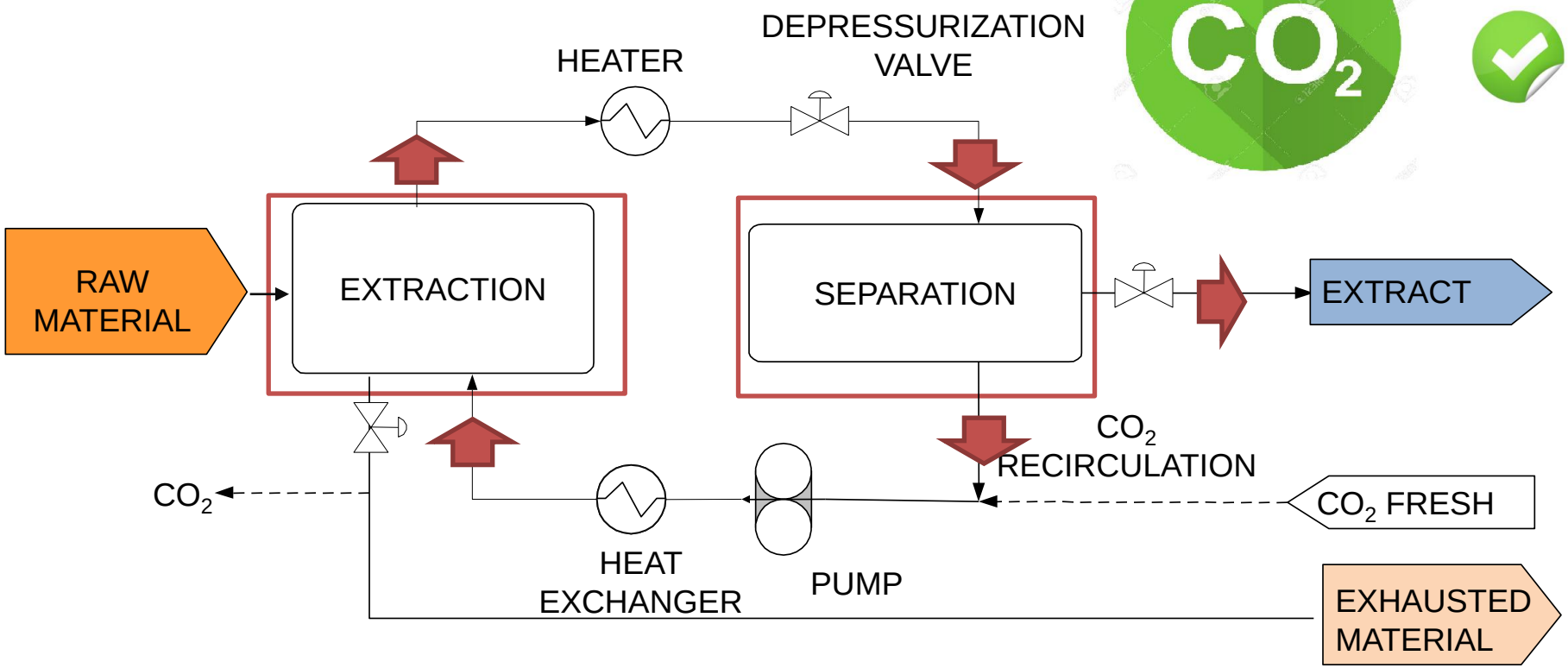
Introduction

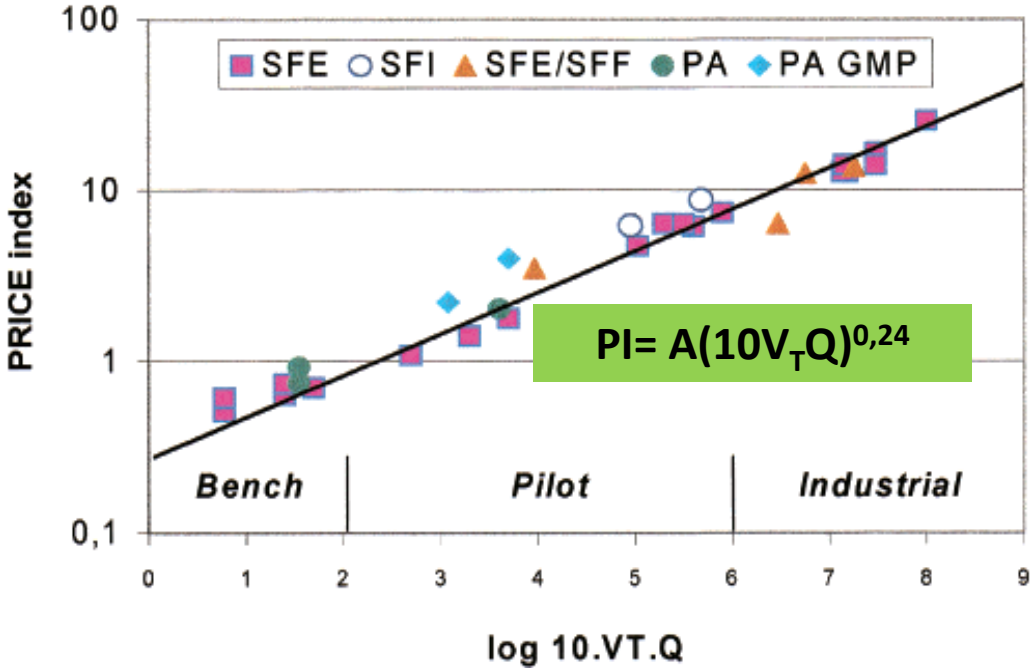
Supercritical Fluid Extraction





Introduction

- A co-solvent/modifier/entrainer is added to a supercritical gas in order to:
  1. Increase solubility
  2. Increase separation factor
  3. Reduce operating pressure (V_T) and CO_2 consumption (Q)



V_T= Total volume of the vessels
Q = CO_2 flowrate

↑ (V_T Q)= ↑OPEX +↑ CAPEX OF THE SFE PROCESSES

Perrut, M. Ind.Eng.Chem.Res., 39(12), 4531–4535 (2000).

Introduction

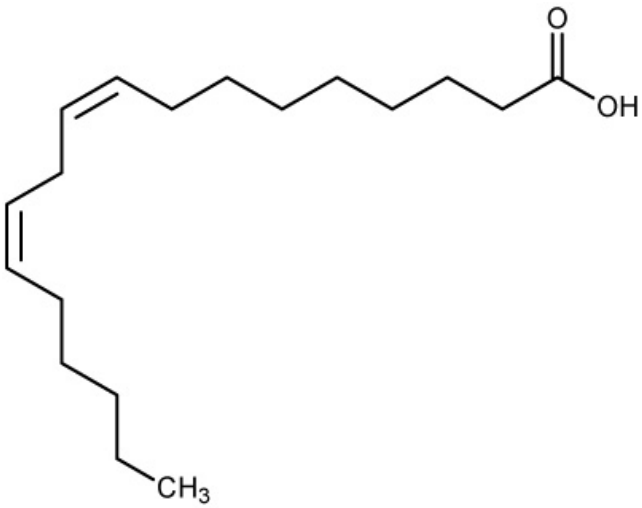
- The co-solvent/modifier/entrainer should :
  - Have volatility between the supercritical solvent and the solute
  - Have higher critical temperature than the supercritical solvent
  - Be used in low concentrations < 10 % g g^{-1}
- However:
  - It increases the critical locus of the mixtures
  - It might contaminate the product, therefore a further separation stage would be needed
  - It should be recovered and reused
  - It should not be toxic. Most frequent ones are ethanol, ethyl acetate, water (low solubility in CO_2)

Objective of this study

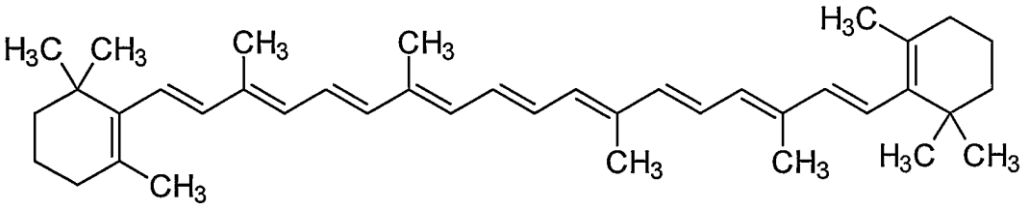
The aim of this study was to predict the best co-solvents to be used with sc-CO_2 using the Hansen solubility theory.

The selection of the best co-solvent requires long and expensive experimental effort.

The work was exemplified on the extraction of some bioactive compounds.



Linoleic acid



β-carotene

Computational Methods

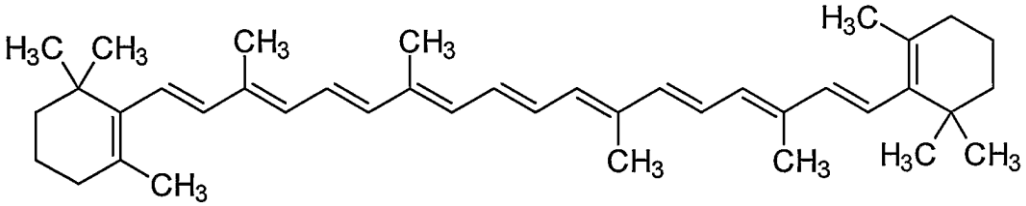
To estimate the HSP of the bioactive compounds

Calculated property	Method used
HSP values from dispersion, polarity and hydrogen bonding forces	Hansen and Beerbower (2007)
Total solubility parameter (δ_T)	Fedors (1974)
Temperature dependence of the HSP compounds	Jayasri and Yaseen (1980)
Critical properties	Joback and Reid (1987)

Computational Methods

HSP of β-carotene

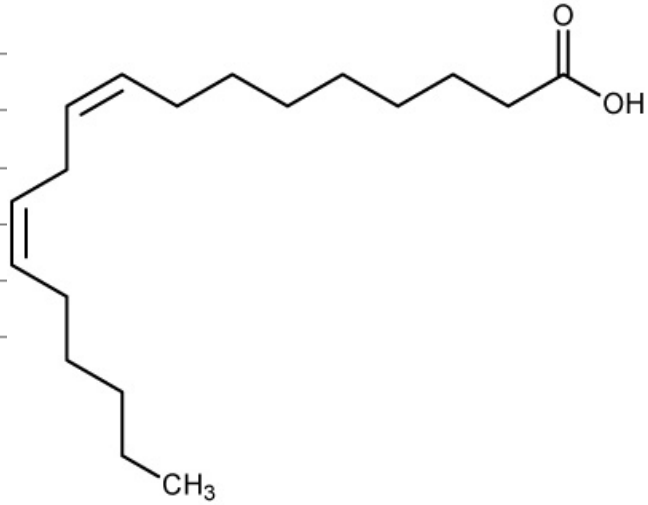
Functional group	Molar Volume [$cm^3\ mol^{-1}$]	δ_d [$MPa^{1/2}$]	δ_p [$MPa^{1/2}$]	δ_h [$MPa^{1/2}$]	δ_T [$MPa^{1/2}$]	Number of functional group
$-CH_3$	33.50	549.99	0.00	0.00	549.99	10
$-CH_2-$	16.10	576.88	0.00	0.00	576.88	6
C- (Sat)	-19.20	171.11	0.00	0.00	171.11	2
-CH=	13.50	427.77	8.80	88.00	503.54	14
=C	-0.50	391.10	29.33	88.00	503.54	8
C-6 (Ring)	16.00	122.22	0.00	0.00	122.22	2
δ_d [$MPa^{1/2}$]						16.18
δ_p [$MPa^{1/2}$]						2.24
δ_h [$MPa^{1/2}$]						5.21
δ_T [$MPa^{1/2}$]						17.01



β-carotene

HSP of linoleic acid

δ_d [$MPa^{1/2}$]	18.29
δ_p [$MPa^{1/2}$]	2.94
δ_h [$MPa^{1/2}$]	7.24
δ_T [$MPa^{1/2}$]	19.82



Linoleic acid

Computational Methods

Prediction of the critical temperature

β-carotene

Functional group	Number of functional groups	T_b [K]	T_c [K]	$\sum T_b$ [K]	$\sum T_c$ [K]
$-CH_3$	10	23.58	0.01	235.80	0.14
$-CH_2-$ (Ring)	6	27.15	0.01	162.90	0.06
-C Sat (Ring)	2	21.32	0.00	42.64	0.01
-CH= (Ring)	14	26.73	0.01	374.22	0.11
-C=	4	24.14	0.01	96.56	0.05
-C= (Ring)	4	31.01	0.01	124.04	0.06
Total	40	153.93	0.06	1036.16	0.43
T_c [K]					1070

Critical temperature of linoleic acid

787 K

GCM by Jayasri and Yaseen (1980)

Computational Methods

Effect of temperature on the HSP of β-carotene

Temperature (K)	δ_d [MPa$^{1/2}$]	δ_p [MPa$^{1/2}$]	δ_h [MPa$^{1/2}$]
303.15	16.15	2.24	5.20
313.15	16.09	2.23	5.18
323.15	16.04	2.22	5.17
333.15	15.98	2.21	5.15
343.15	15.92	2.20	5.13
353.15	15.86	2.20	5.11
363.15	15.80	2.19	5.09
373.15	15.75	2.18	5.07

$$\frac{\delta_2}{\delta_1} = \left(\frac{1 - T_{r2}}{1 - T_{r1}}\right)^{0.34}$$

Computational Methods

HSP of the solvents

Range tested:

Temperatures from 273.15 K to 373.15 K

Pressure from 5 MPa to 60 MPa

$$\frac{\delta_{Dref}}{\delta_D} = \left(\frac{V_{ref}}{V}\right)^{-1.25}$$

$$\frac{\delta_{Pref}}{\delta_P} = \left(\frac{V_{ref}}{V}\right)^{-0.5}$$

$$\frac{\delta_{Href}}{\delta_H} = exp\left[-1.32\ x\ 10^{-3}(T_{ref} - T) - ln\left(\frac{V_{ref}}{V}\right)^{-0.5}\right]$$

$$\sum \text{Total Energy}_{\text{any blend}} = \text{Energy}_{\text{any 1}} + \text{Energy}_{\text{any 2}} + \text{Energy}_{\text{any 3}} + \text{Energy}_{\text{any 4}} \cdots$$

For mixtures

Box A3.1 The Linear Blend Rule

$$\delta_{any} = \sum\{v_i \times [\delta_i]\}$$

Linear Blend rule

The linear blend rule (above) has been used successfully for the past 40 years. It has the merit of simplicity[3] and perhaps the assumptions behind solubility parameters don't warrant a more complex formula.

Durkee, J. Cleaning with Solvents: Science and Technology, William Andrew (2013)

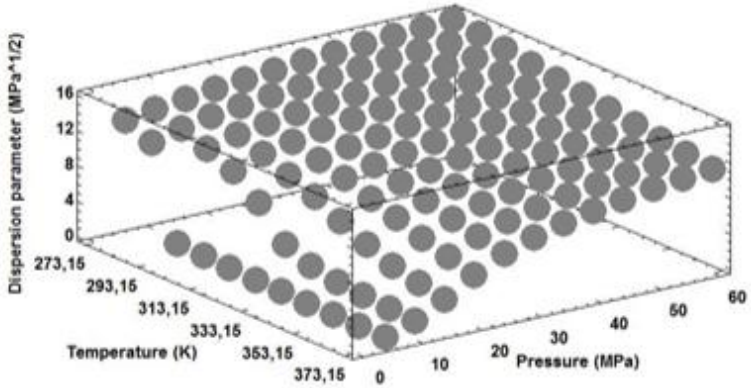
Computational Methods

Critical properties, HSP ref values (Hansen´s handbook) and limiting conditions of the REFPROP model for the determination of molar volume

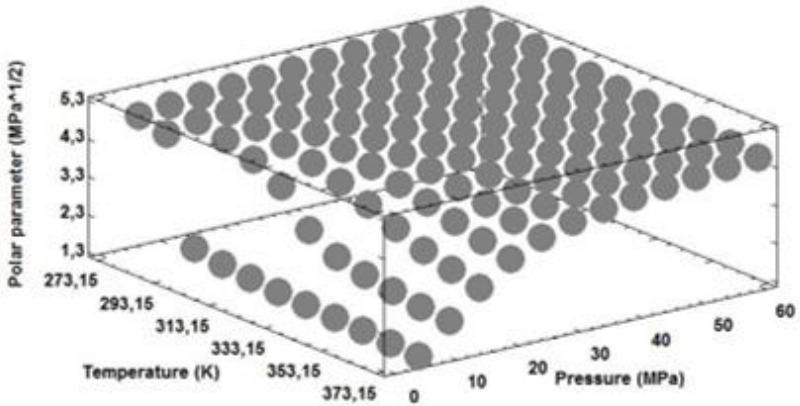
Solvent	Tc/K	Pc/MPa	EOS Limits	δ_{Dref}	δ_{Pref}	δ_{href}	V_{ref}
Water	647.11	22.07	(273.16 – 2000) K, 1000 MPa	15.5	16.0	42.3	18.0
Methanol	512.68	7.95	(175.61 – 620) K, 800 MPa	15.1	12.3	22.3	40.7
CO_2	304.13	7.38	(216.592 -2000) K, 800 MPa	15.6	5.2	5.8	39.1
Ethanol	514.57	6.23	(250 – 650) K, 280 MPa	15.8	8.8	19.4	58.5
Acetone	508.07	4.70	(178.5 – 550) K, 700 MPa	15.5	10.4	7.0	74.0
Diethyl ether	466.78	3.65	(270 – 500) K, 40 MPa	14.5	2.9	5.1	104.8
Benzene	562.02	4.89	(278.7 – 635) K, 78 MPa	18.4	0.0	2.0	89.4
Cyclohexane	553.4	4.07	(279.47 – 700) K, 80 MPa	16.8	0.0	0.2	108.8
n-Hexane	507.55	3.03	(177.83 – 600) K, 100 MPa	14.9	0.0	0.0	131.6

Solubility parameter (δ) in $MPa^{1/2}$ and volume molar in $cm^3\ mol^{-1}$

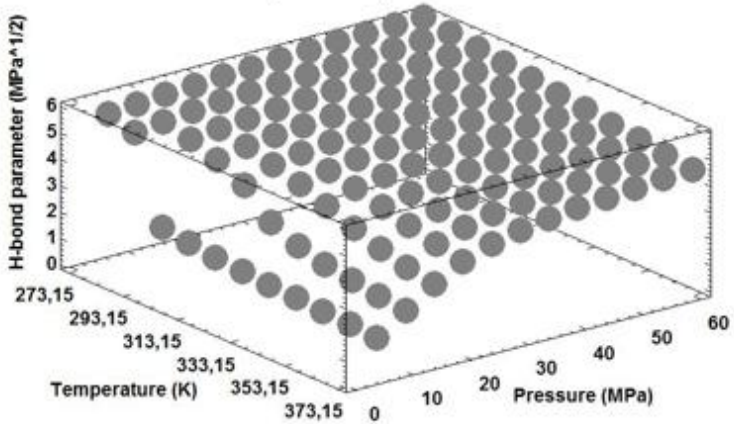
Variation of the HSP of pure CO_2 with operating conditions



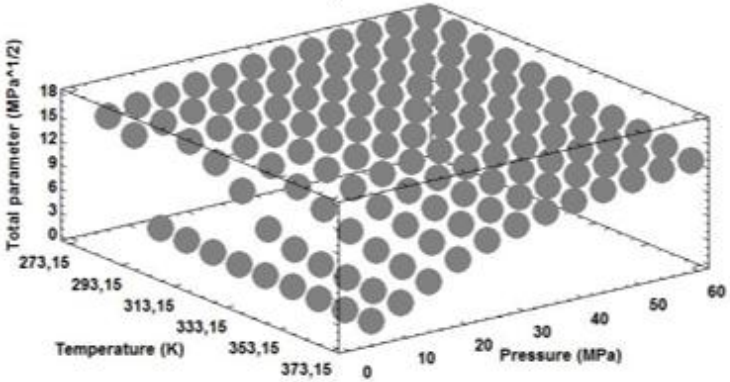
Dispersion parameter



Polar parameter

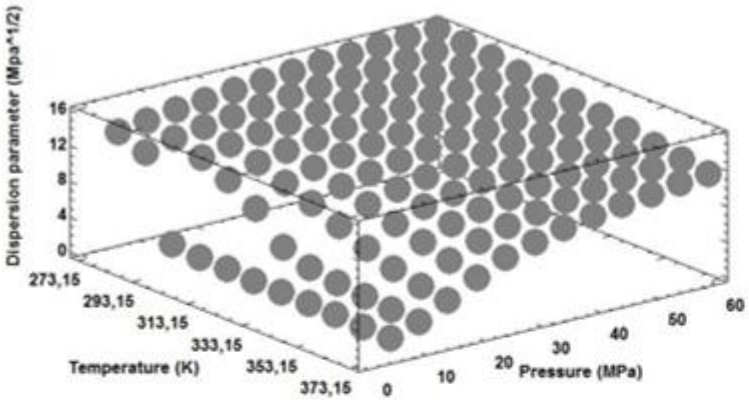


Hydrogen-bonding parameter

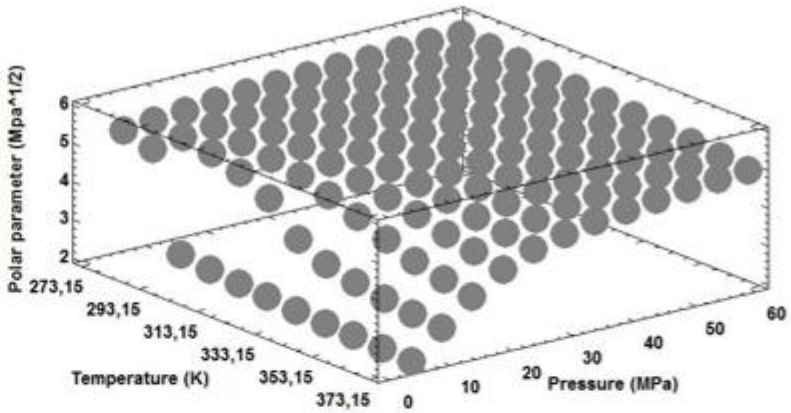


Total solubility parameter

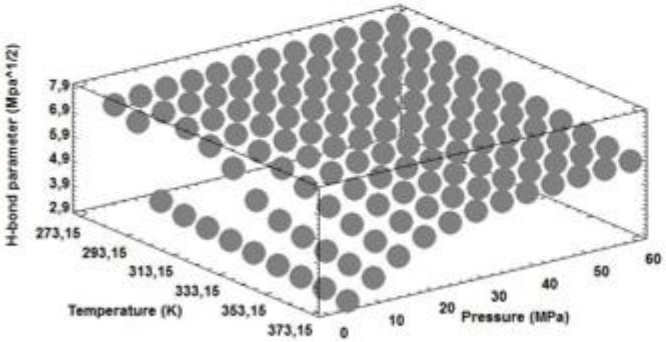
Variation of the HSP of CO_2 /ethanol (90:10 v/v) mixture with operating conditions



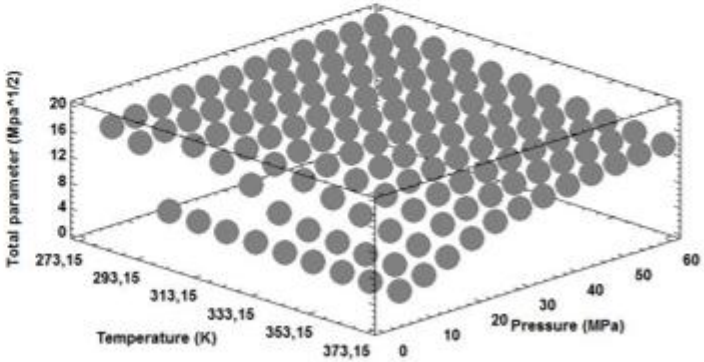
Dispersion parameter



Polar parameter



Hydrogen-bonding parameter



Total solubility parameter

Total (one-component) and HSP values of the mixture of CO_2/ethanol (90:10 v/v)

Computational Methods

Solubility estimation

Solubility predictions were evaluated using the Ra parameter for linoleic acid and RED parameter for β-carotene.

$$R_a = \sqrt{4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2}$$

$$RED = \frac{R_a}{R_0}$$

Solubility data for linoleic acid in organic solvents were not available

Computational Methods

R_a of linoleic acid in pure CO_2

	P [MPa]											
T [K]	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**	**50**	**55**	**60**
273.15	12.52	11.42	10.59	9.90	9.32	8.80	8.34	7.92	7.54	7.18	6.86	6.55
283.15	14.60	12.93	11.84	10.99	10.29	9.69	9.16	8.68	8.25	7.86	7.49	7.16
293.15	34.79	14.75	13.22	12.15	11.31	10.60	10.00	9.46	8.98	8.54	8.14	7.76
303.15	34.89	17.20	14.81	13.41	12.39	11.56	10.86	10.25	9.71	9.22	8.78	8.37
313.15	34.86	21.33	16.67	14.79	13.52	12.54	11.74	11.05	10.45	9.91	9.43	8.98
323.15	34.76	28.04	18.91	16.29	14.71	13.56	12.64	11.86	11.19	10.60	10.07	9.59
333.15	34.63	30.23	21.54	17.92	15.96	14.60	13.54	12.67	11.93	11.28	10.70	10.18
343.15	34.47	31.00	24.14	19.63	17.25	15.65	14.45	13.48	12.66	11.95	11.33	10.76
353.15	34.28	31.36	26.07	21.31	18.54	16.71	15.36	14.28	13.39	12.62	11.94	11.33
363.15	34.08	31.52	27.29	22.81	19.78	17.74	16.25	15.06	14.09	13.26	12.53	11.89
373.15	33.87	31.57	28.04	24.03	20.92	18.73	17.10	15.82	14.77	13.88	13.11	12.42

Computational Methods

R_0 estimation for β-carotene

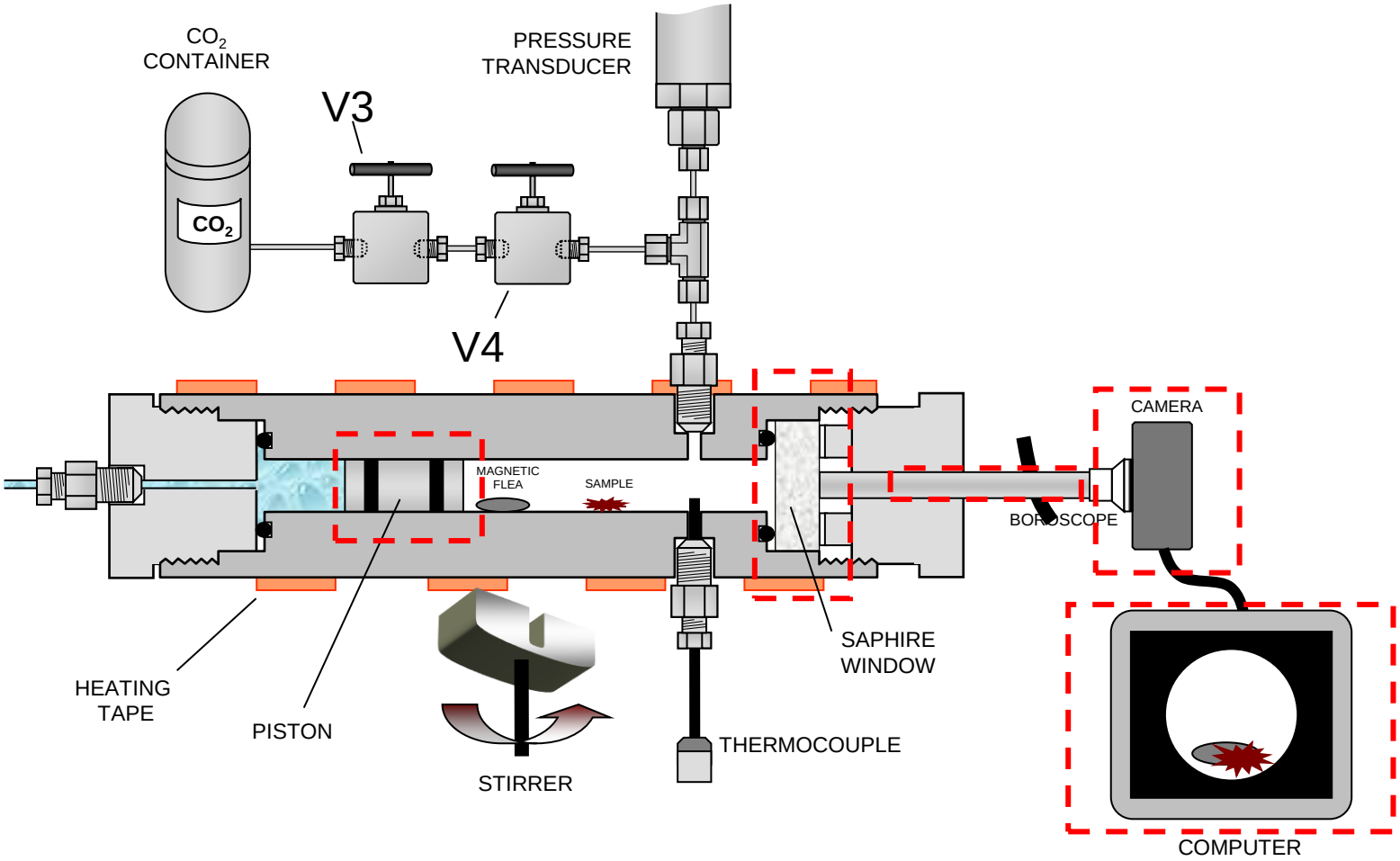
	δ_d	δ_p	δ_h	R_0
β-carotene	16.18	2.24	5.21	8.47

Solvents	δ_d	δ_p	δ_h	V	Score	R_a	RED
Acetone	15.50	10.40	7.00	74.00	1.00	8.46	1.00
Acetonitrile	15.30	18.00	6.10	52.60	0.00	15.88	1.88
Benzene	18.40	0.00	2.00	89.40	1.00	5.92	0.70
Chloroform	17.80	3.10	5.70	80.70	1.00	3.39	0.40
Cyclohexane	16.80	0.00	0.20	108.70	1.00	5.63	0.66
Cyclohexanone	17.80	6.30	5.10	104.00	1.00	5.20	0.61
Dimethyle formamide (DMF)	17.40	13.70	11.30	77.00	0.00	13.20	1.56
Dimethyle sulfoxide (DMSO)	18.40	16.40	10.20	71.30	0.00	15.66	1.85
Ethanol	15.80	8.80	19.40	58.60	0.00	15.65	1.85
Ethyl Acetate	15.80	5.30	7.20	98.50	1.00	3.73	0.44
Ethyl ether	19.00	7.40	4.10	79.40	1.00	7.72	0.91
Hexane	14.90	0.00	0.00	131.60	1.00	6.22	0.73
Isopropyl alcohol	15.80	6.10	16.40	76.80	0.00	11.86	1.40
Methanol	15.10	12.30	22.30	40.70	0.00	19.95	2.36
Methyl ethyl ketone (2-butanone)	15.30	6.10	4.10	125.80	1.00	4.39	0.52
Tetrahydrofuran (THF)	16.80	5.70	8.00	81.70	1.00	4.61	0.54
Toluene	18.00	1.40	2.00	106.60	1.00	4.93	0.58

Validation of the predictions with experimental data obtained by static method

Materials & Methods

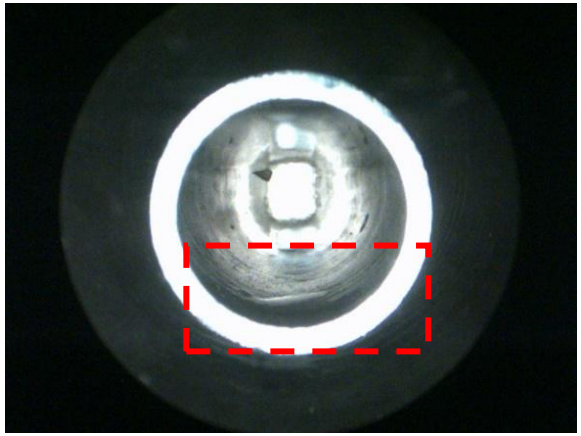
Installation: variable volume view cell



The Journal of Supercritical Fluids, 46(3), 238–244 (2008).

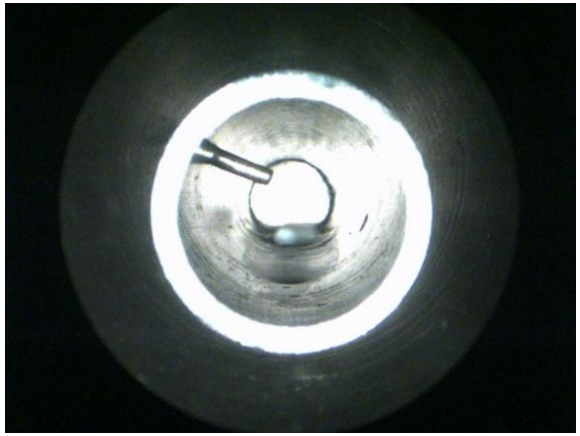
Results & Discussion

Solubility of linoleic acid in pure CO_2



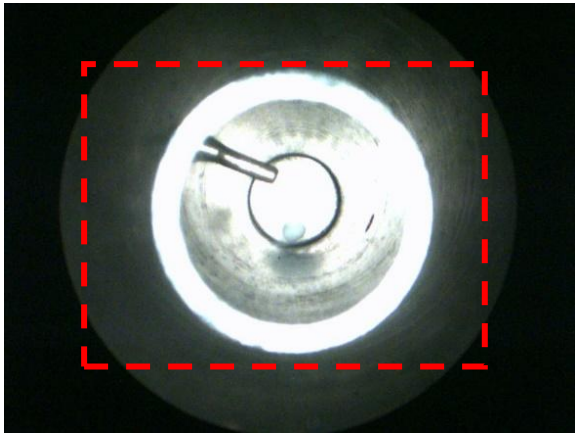
7 MPa, 298.15 K

↑P

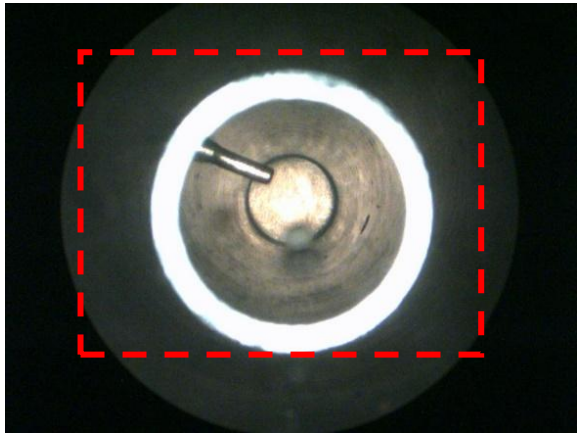


17 MPa 313.15 K

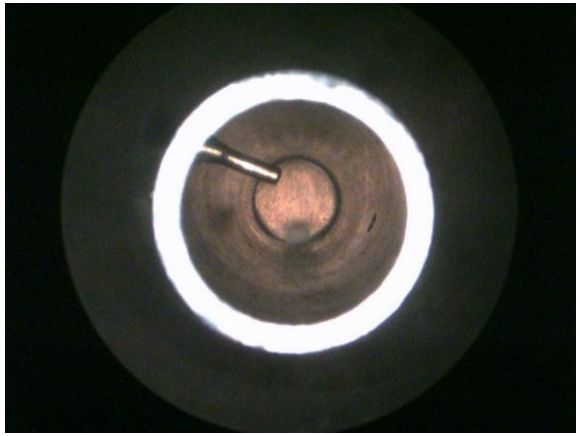
↑P



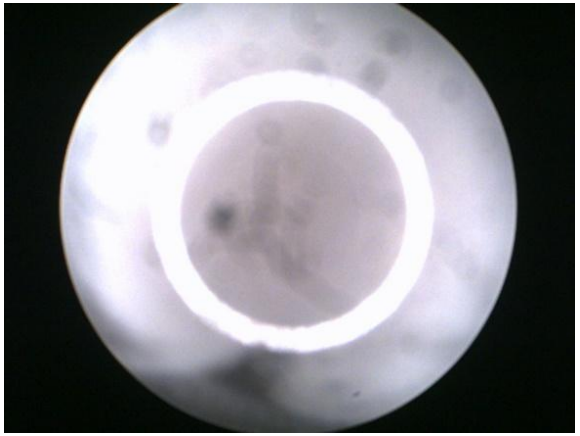
25 MPa, 313.15 K



↓P 22.2 MPa, 313.15 K (cloud point)



↓P 18 MPa, 310.15 K



↓P 15 MPa, 308.15 K

Results & Discussion

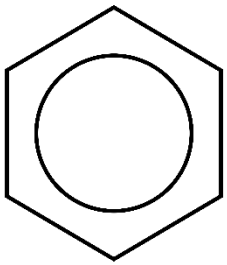
Solvent capacity (Ra) of CO_2-cosolvent mixtures at 313.15 K and increasing pressures predicted by Hansen theory

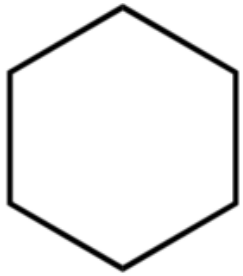
Ranking	System	Tc/K	Pc/MPa	Ra at 10 MPa	Ra at 20 MPa
1	CO_2 + Benzene	322.98	8.55	20.202	13.962
2	CO_2 + Cyclohexane	322.75	9.05	20.369	14.129
3	CO_2 + Ethanol	315.2	8.61	20.370	14.146
4	CO_2 + Water	Very high CP		20.407	14.231
5	CO_2 + Methanol	311.70	8.27	20.432	14.220
6	CO_2 + acetone	323.15	8.94	20.478	14.262
7	CO_2 + Hexane	316.80	8.49	20.550	14.302
8	CO2 + Diethyl ether	Not found		20.559	14.313
9	Pure CO2	304.13	7.3773	21.249	14.707
CO2 (1) + co-solvent (2) (X1 ≈ 0.95)					

Results & Discussion

Equilibrium pressure obtained by static method

Ranking	System	Equilibrium pressure/MPa	
		313.15 K	323.15 K
1	CO_2 + Benzene	16.3 ± 0.1	18.0 ± 0.1
2	CO_2 + Cyclohexane	17.4 ± 0.2	19.7 ± 0.2
3	CO_2 + Ethanol	9.7 ± 0.2	12.5 ± 0.2
4	CO_2 + Methanol	10.6 ± 0.0	13.7 ± 0.2
5	CO_2 + acetone	12.2 ± 0.1	14.4 ± 0.1
6	CO_2 + Hexane	15.6 ± 0.1	18.5 ± 0.1
7	CO_2 + Diethyl ether	17.5 ± 0.2	19.5 ± 0.2
8	Pure CO_2	22.2 ± 0.1	23.0 ± 0.1
≈ 20 g of sample/kg of solvent and CO_2 + co-solvent (95:05 w/w)			





Results & Discussion

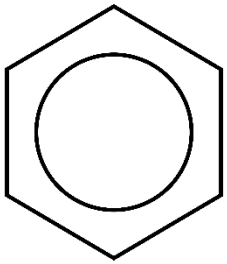
Solvent capacity (Ra) of CO_2-cosolvent mixtures at 313.15 K and increasing pressures predicted by Hansen theory

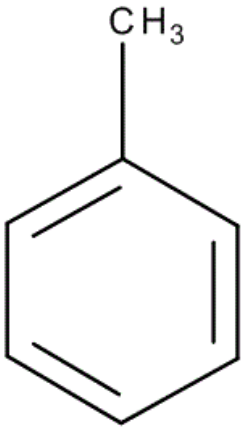
Ranking	System	Tc/K	Pc/MPa	Ra at 10 MPa	Ra at 20 MPa
1	CO_2 + Benzene	322.98	8.55	20.202	13.962
2	CO_2 + Toluene	Not found		20.322	14.087
3	CO_2 + Cyclohexane	322.75	9.05	20.369	14.129
4	CO_2 + Ethanol	315.2	8.61	20.370	14.146
5	CO_2 + Methanol	311.70	8.27	20.432	14.220
6	CO_2 + acetone	323.15	8.94	20.478	14.262
7	CO_2 + Hexane	316.80	8.49	20.550	14.302
8	CO2 + Diethyl ether	Not found		20.559	14.313
9	Pure CO2	304.13	7.3773	21.249	14.707
CO2 (1) + co-solvent (2) (X1 ≈ 0.95)					

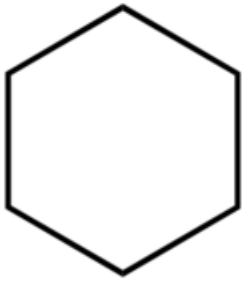
Results & Discussion

Equilibrium pressure obtained by static method

Ranking	System	Equilibrium pressure/MPa	
		313.15 K	323.15 K
1	CO_2 + Benzene	16.3 ± 0.1	18.0 ± 0.1
2	CO_2 + Toluene	18.0 ± 0.1	22.7 ± 0.2
3	CO_2 + Cyclohexane	17.4 ± 0.2	19.7 ± 0.2
4	CO_2 + Ethanol	9.7 ± 0.2	12.5 ± 0.2
5	CO_2 + Methanol	10.6 ± 0.0	13.7 ± 0.2
6	CO_2 + acetone	12.2 ± 0.1	14.4 ± 0.1
7	CO_2 + Hexane	15.6 ± 0.1	18.5 ± 0.1
8	CO_2 + Diethyl ether	17.5 ± 0.2	19.5 ± 0.2
9	Pure CO_2	22.2 ± 0.1	23.0 ± 0.1
≈ 20 g of sample/kg of solvent and CO_2 + co-solvent (95:05 w/w)			







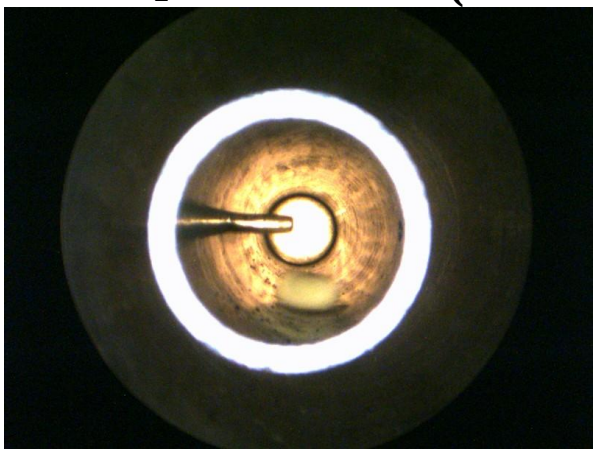
Results & Discussion

Co-solvent power ranked by RED

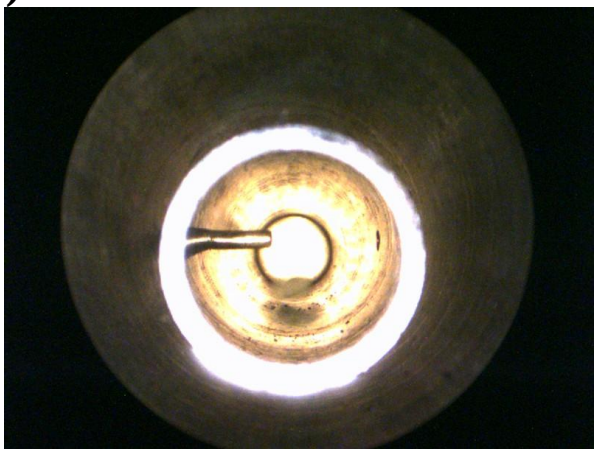
1. Benzene
2. Cyclohexane
3. Ethanol
4. n-Hexane
5. Acetone
6. Methanol
7. Diethyl ether
8. Water.

Solubility of β-carotene at NTP		
Solvent	**Solubility [mg/L]**	**RED**
n-Hexane	600	0.73
Acetone	200	1.00
Ethanol	30	1.84
Methanol	10	2.35

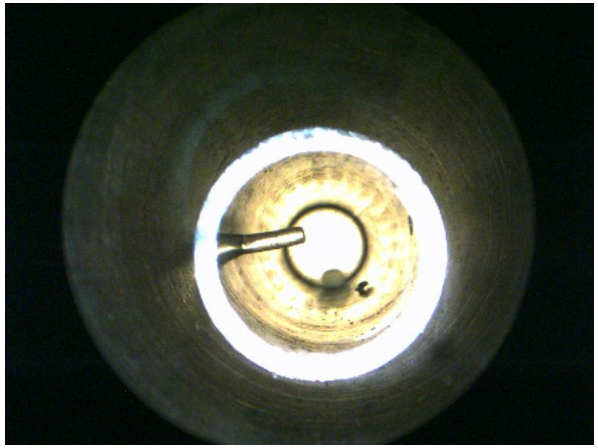
CO_2 + co-solvents (95:05 v/v) at 313.15 K and 15 MPa



CO_2 + Ethanol



CO_2 + Hexane



CO_2 + Acetone

Results & Discussion

RED of β-carotene in pure CO_2 as function of the pressure and temperature

	P [MPa]											
T [K]	5	10	15	20	25	30	35	40	45	50	55	60
273.2	0.96	0.84	0.75	0.68	0.62	0.57	0.53	0.49	0.46	0.44	0.41	0.40
283.2	1.21	1.02	0.89	0.80	0.73	0.67	0.61	0.57	0.53	0.49	0.46	0.44
293.2	3.56	1.23	1.06	0.94	0.85	0.77	0.71	0.65	0.60	0.56	0.52	0.49
303.2	3.59	1.53	1.25	1.09	0.98	0.89	0.81	0.74	0.69	0.64	0.59	0.55
313.2	3.60	2.02	1.48	1.26	1.12	1.01	0.92	0.84	0.78	0.72	0.67	0.62
323.2	3.60	2.82	1.75	1.45	1.27	1.14	1.03	0.94	0.87	0.80	0.75	0.70
333.2	3.60	3.09	2.07	1.65	1.42	1.27	1.15	1.05	0.96	0.89	0.83	0.77
343.2	3.59	3.19	2.39	1.86	1.59	1.40	1.26	1.15	1.06	0.98	0.91	0.85
353.2	3.59	3.25	2.63	2.07	1.75	1.54	1.38	1.26	1.15	1.07	0.99	0.92
363.2	3.58	3.28	2.79	2.26	1.91	1.67	1.50	1.36	1.25	1.15	1.07	1.00
373.2	3.57	3.30	2.89	2.42	2.06	1.80	1.61	1.46	1.34	1.24	1.15	1.07

0-0.2	Highly soluble
0.2-0.4	
0.4-0.6	
0.6-0.8	
0.8-1	
>1	Insoluble

Results & Discussion

Extraction of β-carotene from *Dunaliella salina* using supercritical CO_2

J. Agric. Food Chem., 55, 10585–10590 (2007).

Pressure from 18.27 to 43.73 MPa
Temperatures from 282.95 K to 313.15 K

The highest yield of β-carotene was obtained at the **highest pressure** tested (43.73 MPa) and a **low temperature** (300.65 K).

3.751 mg β-carotene/100 mg extract were extracted under these conditions.

Results & Discussion

Comparison of the RED values of β-carotene in CO_2 and CO_2/ethanol (95:05 v/v) mixture

T [K] / P [MPa]	Pure CO_2					
	10	20	30	40	50	60
273.15	0.83	0.67	0.56	0.49	0.43	0.40
283.15	1.01	0.80	0.66	0.56	0.49	0.44
293.15	1.23	0.94	0.77	0.65	0.56	0.49
303.15	1.53	1.10	0.89	0.75	0.64	0.56
313.15	2.03	1.27	1.01	0.85	0.72	0.63
323.15	2.82	1.46	1.14	0.95	0.81	0.70
333.15	3.10	1.66	1.28	1.06	0.90	0.78
343.15	3.21	1.88	1.42	1.17	0.99	0.86
353.15	3.27	2.09	1.56	1.28	1.09	0.94
363.15	3.30	2.29	1.70	1.39	1.18	1.02
373.15	3.33	2.45	1.83	1.49	1.27	1.10

T [K] / P [MPa]	CO_2 + Ethanol (95:05 v/v)					
	10	20	30	40	50	60
273.15	0.82	0.67	0.58	0.51	0.47	0.44
283.15	0.98	0.78	0.66	0.57	0.51	0.47
293.15	1.19	0.91	0.76	0.65	0.57	0.51
303.15	1.46	1.05	0.86	0.73	0.63	0.56
313.15	1.93	1.21	0.97	0.82	0.70	0.62
323.15	2.68	1.39	1.09	0.91	0.78	0.68
333.15	2.93	1.58	1.22	1.01	0.86	0.75
343.15	3.04	1.78	1.34	1.11	0.94	0.82
353.15	3.09	1.98	1.47	1.21	1.03	0.89
363.15	3.12	2.16	1.60	1.30	1.11	0.96
373.15	3.14	2.31	1.72	1.40	1.19	1.03

Conditions where pure CO_2 is better solvent

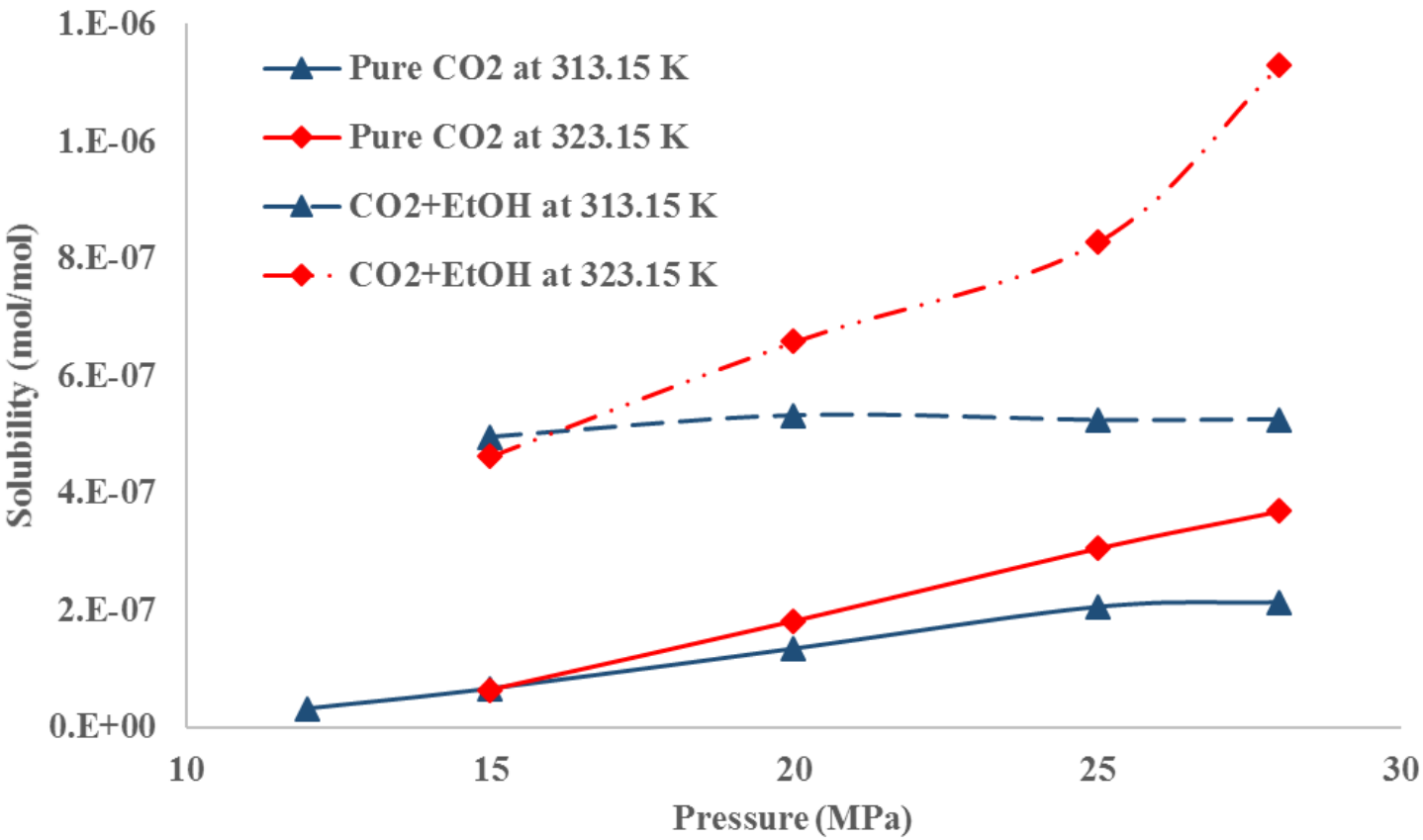
T [K] / P [MPa]	RED pure CO2 - RED mixture					
	10	20	30	40	50	60
273.15	0.01	0.00	-0.01	-0.02	-0.03	-0.04
283.15	0.03	0.01	0.00	-0.01	-0.02	-0.03
293.15	0.05	0.03	0.01	0.00	-0.01	-0.02
303.15	0.07	0.04	0.03	0.02	0.01	0.00
313.15	0.10	0.06	0.04	0.03	0.02	0.01
323.15	0.15	0.07	0.05	0.04	0.03	0.02
333.15	0.16	0.09	0.06	0.05	0.04	0.03
343.15	0.17	0.10	0.08	0.06	0.05	0.04
353.15	0.18	0.11	0.09	0.07	0.06	0.05
363.15	0.18	0.13	0.10	0.08	0.07	0.06
373.15	0.18	0.14	0.11	0.09	0.08	0.07

Conditions where CO_2 + ethanol is better solvent

Results & Discussion

Solubility of β-carotene in both pure and ethanol-modified CO_2 (2.4 %)

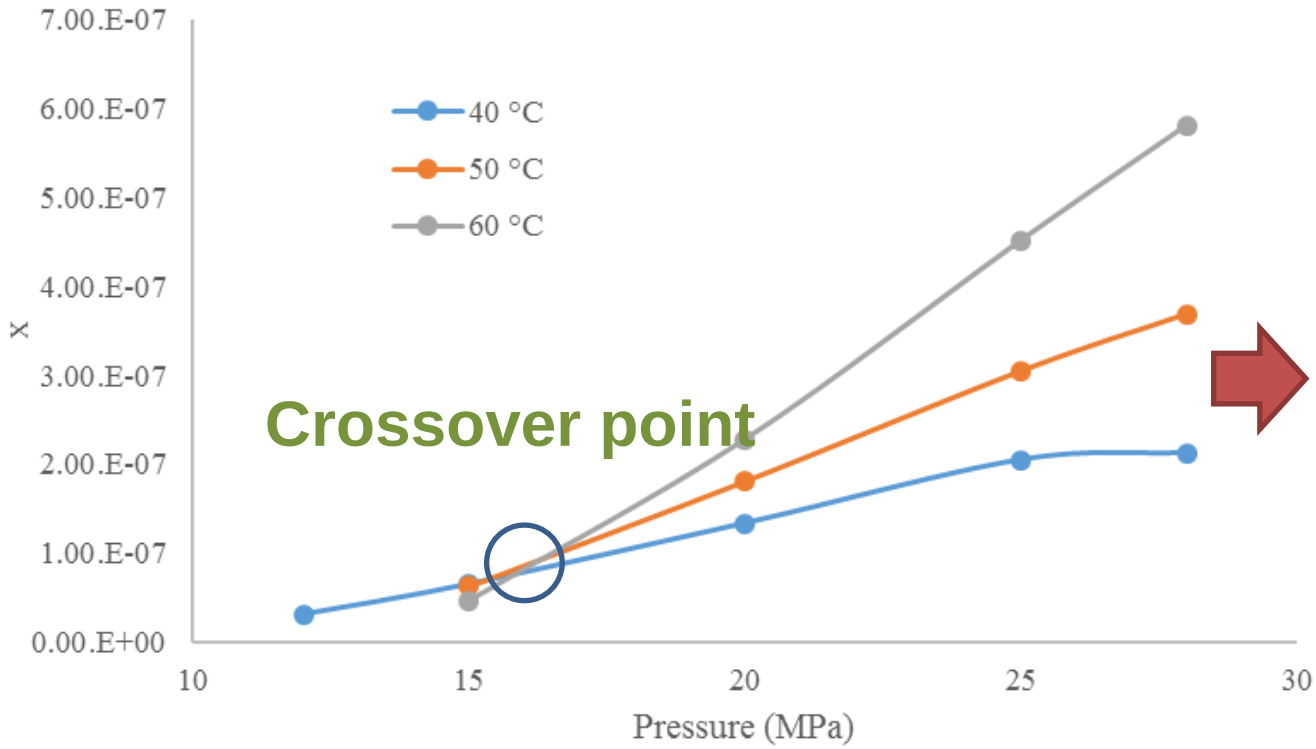
The presence of ethanol enhances the solubility and its dependence with pressure



J. Supercrit. Fluids., 21, 195–203 (2001).

Results & Discussion

Solubility of β-carotene in pure CO_2



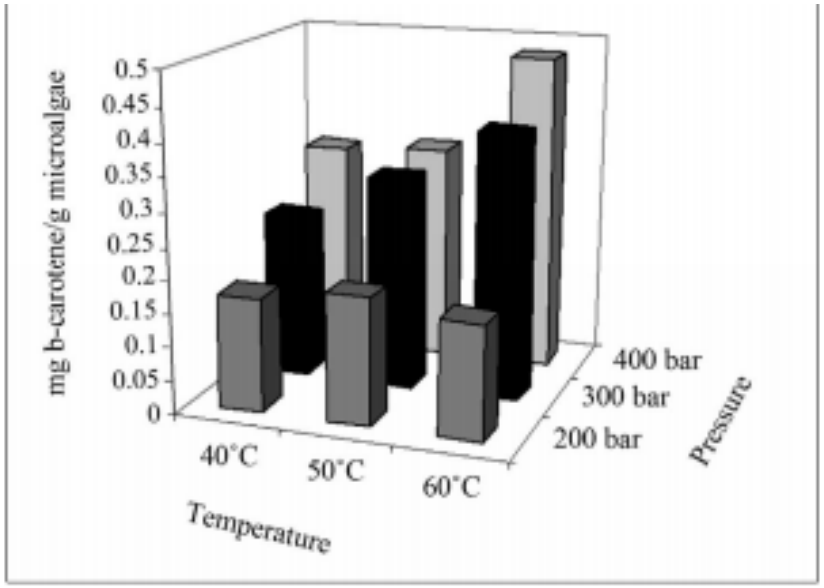
Hansen's theory does not consider the effect of temperature on the vapour pressure of the solute

J. Supercrit. Fluids., 21, 195–203 (2001).

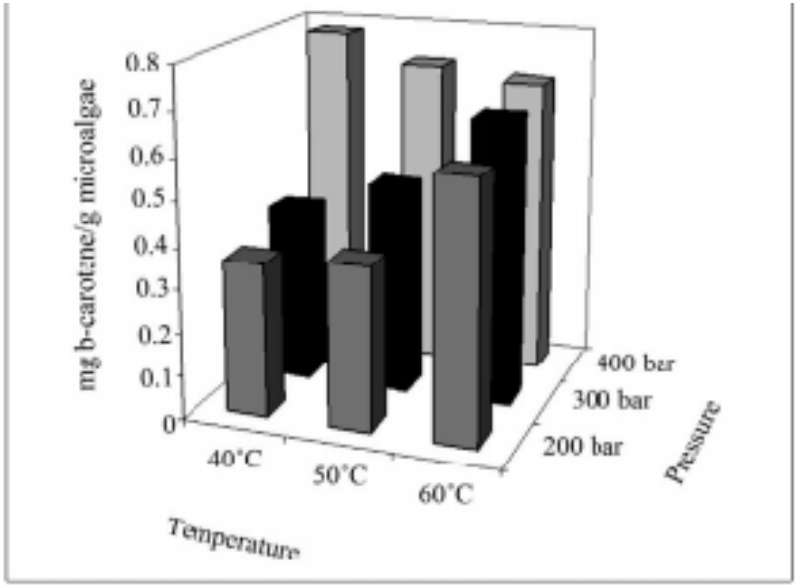
Results & Discussion

Experimental results on the extraction of β-carotene from *Synechococcus* sp. in CO_2 and mixture with ethanol

Pure CO_2



CO_2 + Ethanol (95:05 v/v)



Extraction yields of *β*-carotene.

Supercritical extraction from solids is controlled by internal mass transfer and so enhanced by temperature

Summary & Conclusions

- ✓ The Hansen theory can be used to compare the performance of co-solvents in the solubility of natural compounds in a specific interval of operating conditions
  - Caution should be taken with solvents with a ring structure
- ✓ The effect of pressure is well predicted due to the direct relation between pressure and density
- ✓ A contribution of the impact of temperature on solute vapour pressure should be added to the model, e.g. a term with the Antoine equation?
- ✓ The mass transfer kinetics should be taken into account when using the theory to predict the supercritical extraction of bioactive compounds from solids

Thank you for your attention

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Application of the Hansen solubility theory for the selection of co-solvents for supercritical carbon dioxide extraction

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