

Solubility of β -Carotene in Dense Carbon Dioxide and Nitrous Oxide from 308 to 323 K and from 9.6 to 30 MPa

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A one-pass flow system was used to measure the solubilities of β -carotene ($C_{40}H_{56}$) in dense carbon dioxide and nitrous oxide. The solubilities established at 308, 313, 318, and 323 K and pressures ranging from 9.6 to 30 MPa were correlated with the temperature and the density of pure solvent. The equation proposed by Chrastil was used for the correlation with successful results.

Introduction

β -Carotene is a hydrocarbon carotenoid and widely distributed in plant and animal tissues. This coloring matter has been noted for its anticancer properties as well as its nutritional functions.

Supercritical fluids have been used for isolating natural products such as flavors and lipids (1-3). Carbon dioxide (CO_2) has been commonly employed as an extracting solvent because of its low toxicity, safety, and low critical temperature (304 K), and the solubility data in supercritical CO_2 have been reported for various substances (4-7). Cygnarowicz et al. (8) have measured the solubilities of β -carotene in supercritical CO_2 with and without cosolvents.

K.S. and others have reported that nitrous oxide (N_2O) shows higher affinity to lipids than CO_2 does (9, 10). In this study, the solubilities of β -carotene in dense CO_2 and N_2O were measured and the obtained data were correlated with temperature and gas density by applying the equation proposed by Chrastil (11).

Experimental Section

A schematic diagram of the apparatus consisting of the extracting system and the chromatographic system is shown in Figure 1. β -Carotene with 96% purity (purchased from Sigma Chemical Co.) was dissolved in hexane, and the solution was evaporated together with alumina beads with a mean diameter of 2.0 mm. After the above procedure β -carotene was in the amorphous state. The beads supporting β -carotene on their surface were packed into the extraction cell which was a stainless steel pipe of 20-cm path length and 0.8-cm internal diameter. Extracting pressures were controlled by a back-pressure regulator (Tescom 26-3220-20). The gas flow rate was regulated by a metering valve (Whitey SS-22RS2) and monitored with a flow meter. In this study, the flow rate was adjusted around 50 mL/min, which corresponded to 30-50 min of residence time. The fluid saturated with β -carotene emerged from the cell and passed through a switching valve equipped with a sample loop. The internal volumes of the used loops were 100 μ L on the measurement employing CO_2 and 20 μ L on the one employing N_2O . The extraction cell and the sample loop were placed in the column oven whose temperature could be controlled to ± 0.1 K. The fluid in the loop was introduced to the chromatographic system by switching the six-way valve. The dissolving β -carotene passed through the packed column and was detected with a UV/vis detector fitted with a high-pressure cell (Jasco 875-UV). The output of the detector was

monitored by a chart recorder, and the net weight of β -carotene in the loop was determined from the peak area of the obtained chart by use of the calibration curve which was previously prepared in the following way. The β -carotene solutions of known concentration were prepared in chloroform, and 20 μ L of each solution was injected into the above-mentioned chromatographic system. The chart of UV absorption of β -carotene was obtained for each solution in this way, and the calibration curve was provided by the plot of peak area vs weight of β -carotene. The chromatographic system was provided in order to check the purity of dissolved β -carotene because it is labile against light and heat. The chromatographic conditions were as follows: column, Cosmosil C18-AR (5 μ m, 150 \times 4.6 mm i.d., Nacal tesque); mobile phase, CO_2 ; temperature, 313 K; back-pressure, 19.6 MPa; flow rate, 2.5 g/min; detection wavelength, 450 nm. Solubilities were measured at 308, 313, 318, and 323 K, and in the pressure range of 9.6-30 MPa.

Melting point and enthalpy of fusion of β -carotene were also measured by a differential scanning calorimeter (Perkin-Elmer DSC7) in order to evaluate the variation of solubility caused by the state of the solid (crystalline or amorphous).

Results and Discussion

Solubility Data. The experimental solubility values for β -carotene in CO_2 and N_2O are presented in Table I. These data are also presented in Figure 2. The reproducibility of the solubilities was within 10%. The larger errors were obtained at the low pressures because of low absorbance. The densities of CO_2 and N_2O given in Table I were obtained from experimental data reported previously (12, 13). Nitrous oxide is the better solvent for β -carotene than CO_2 . The experimental data were rearranged by the application of the following equation proposed by Chrastil (11):

$$\ln S = k \ln \rho - \Delta H/RT + q - \ln ([1000M_B]^k / [M_A + kM_B]) \quad (1)$$

where S is the solubility of the solute, ρ is the gas density, k is the number of gas molecules associating with one molecule of solute to form a solvatocomplex, $\Delta H (= \Delta H_{\text{soln}} + \Delta H_{\text{vap}})$ is the total reaction enthalpy (enthalpy of solvation plus enthalpy of vaporization of the solute), q is a constant, and M_A and M_B are the molecular weights of the solute and the gas, respectively.

Figure 3 shows the relation between solubility and reciprocal temperature at the given gas densities, 700 and 800 kg/m^3 . The data follow straight lines, and the slopes give the enthalpy values, ΔH in eq 1. The determined enthalpy values were shown in Table II. The solubility data were also plotted as a function of gas density in Figure 4. The log-log plots of solubility versus gas density at given temperatures were found to be linear, and the slopes give the k values in eq 1. The determined k values are represented in Table II. The constant

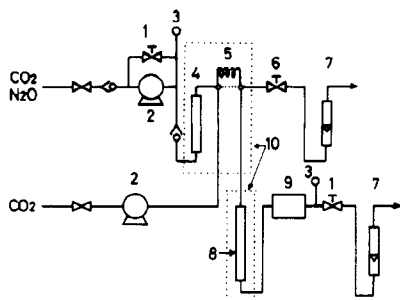


Figure 1. Schematic diagram of the apparatus: (1) back-pressure regulator; (2) pump; (3) pressure gauge; (4) extraction cell; (5) sample valve; (6) metering valve; (7) flow meter; (8) packed column; (9) UV/vis detector; (10) column oven.

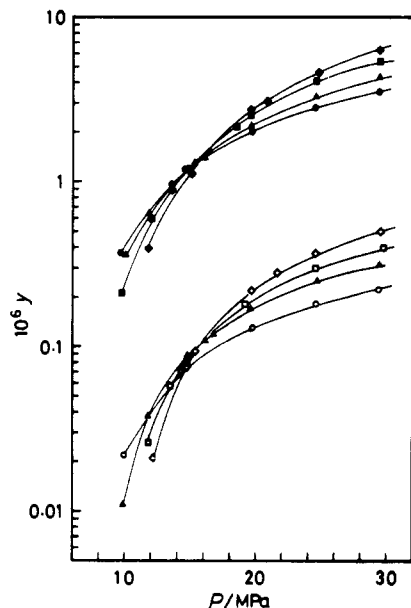


Figure 2. Solubility of β -carotene in CO_2 and N_2O . CO_2 : \circ , 308 K; Δ , 313 K; \square , 318 K; \diamond , 323 K. N_2O : \bullet , 308 K; \blacktriangle , 313 K; \blacksquare , 318 K; \blacklozenge , 323 K.

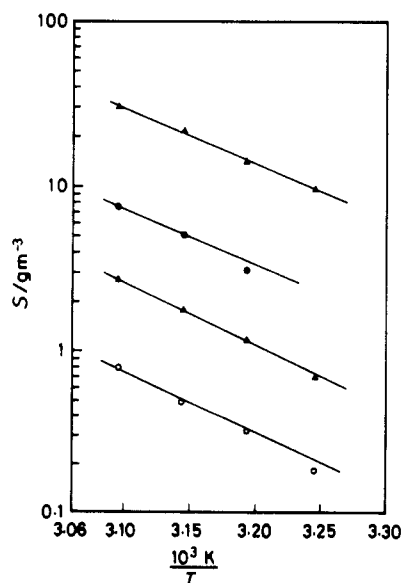


Figure 3. Solubility S versus reciprocal temperature at various gas densities. CO_2 : \circ , 700 kg m^{-3} ; Δ , 800 kg m^{-3} . N_2O : \bullet , 700 kg m^{-3} ; \blacktriangle , 800 kg m^{-3} .

$b (= q - \ln ([1000M_B]^k / [M_A + kM_B]))$ was decided so as to minimize the sum of the deviation of experimental data from

Table I. Experimental Solubility S of β -Carotene in Dense CO_2 and N_2O

T/K	P/MPa	$\rho/(\text{kg m}^{-3})$	S		
			g m^{-3}	$10^6 y$	
308	9.95	CO_2 700	0.18	0.022	
	14.3	800	0.70	0.071	
	19.8	862	1.4	0.13	
	24.6	899	1.9	0.18	
	29.4	928	2.4	0.22	
	9.87	616	0.085	0.011	
	11.8	700	0.32	0.038	
	14.8	770	0.82	0.087	
	16.1	790	1.0	0.11	
	16.8	800	1.2	0.12	
313	19.6	833	1.7	0.17	
	24.7	878	2.7	0.25	
	29.5	909	3.5	0.32	
	11.8	639	0.20	0.026	
	13.5	700	0.49	0.058	
	14.8	729	0.74	0.083	
	19.2	800	1.8	0.18	
	24.6	853	3.1	0.30	
	29.8	889	4.4	0.40	
	323	12.2	590	0.15	0.021
14.7		684	0.63	0.075	
15.4		700	0.80	0.094	
19.7		776	2.1	0.22	
21.7		800	2.7	0.28	
24.6		828	3.7	0.37	
29.5		867	5.3	0.50	
308		9.64	N_2O 740	3.4	0.37
		13.6	800	9.5	0.97
		14.6	812	1.2×10	1.2
	19.7	856	2.1×10	2.0	
	24.6	887	3.0×10	2.8	
	29.4	910	3.9×10	3.5	
	10.1	700	3.1	0.36	
	11.9	741	5.9	0.65	
	15.3	791	1.2×10	1.3	
	16.1	800	1.4×10	1.4	
313	19.6	834	2.2×10	2.2	
	24.7	868	3.5×10	3.3	
	29.5	893	4.7×10	4.3	
	9.88	620	1.6	0.21	
	12.1	700	5.1	0.60	
	14.8	754	1.1×10	1.2	
	18.5	800	2.2×10	2.2	
	19.6	810	2.5×10	2.6	
	24.6	850	4.1×10	4.0	
	29.5	876	5.8×10	5.4	
323	11.9	647	3.1	0.39	
	13.6	700	7.6	0.89	
	15.1	726	9.9	1.1	
	19.7	789	2.6×10	2.7	
	20.9	800	3.0×10	3.1	
	24.8	831	4.6×10	4.6	
	29.5	860	6.6×10	6.3	

Table II. Solubility Constants for β -Carotene in CO_2 and N_2O

gas	k	$\Delta H/(\text{J mol}^{-1})$	b^a
CO_2	9.3	7.2×10^4	-34.28
N_2O	10.9	6.3×10^4	-45.93

$$^a b = q - \ln ([1000M_B]^k / [M_A + kM_B]).$$

the values calculated by eq 1. As a result, the solubility of β -carotene is expressed as follows:

$$\ln (S/(\text{g m}^{-3})) = 9.3 \ln (\rho/(\text{kg m}^{-3})) - \frac{7.2 \times 10^4}{RT} - 34.28 \quad (\text{in } \text{CO}_2)$$

$$= 10.9 \ln (\rho/(\text{kg m}^{-3})) - \frac{6.3 \times 10^4}{RT} - 45.93 \quad (\text{in } \text{N}_2\text{O}) \quad (2)$$

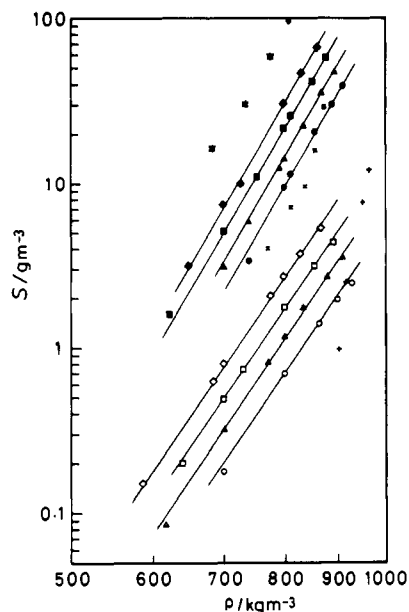


Figure 4. Solubility S of β -carotene in CO_2 and N_2O . Present work, CO_2 : \circ , 308 K; \triangle , 313 K; \square , 318 K; \diamond , 323 K. Present work, N_2O : \bullet , 308 K; \blacktriangle , 313 K; \blacksquare , 318 K; \blacklozenge , 323 K. Cygnarowicz et al. (8), CO_2 : $+$, 313 K; \times , 333 K; $*$, 343 K. The curves are calculated from eq 2.

Table III. Melting Point T_m and Enthalpy of Fusion ΔH_{fus} for β -Carotene

state	T_m/K	$\Delta H_{\text{fus}}/(\text{J mol}^{-1})$
crystalline	456	5.6×10^4
amorphous	454	4.1×10^4

In Figure 4, the data of Cygnarowicz et al. (8) were also plotted. Their data do not agree much with the present data, and in particular, the data at 343 K are much larger than predicted by eq 2. As to this disagreement, the following two reasons are possible. One is that they used crystalline β -carotene for the solubility measurement. The other is that eq 2 was not applicable to the solubility at high temperature because it was determined from the data at 308–323 K and 9.6–30 MPa.

Enthalpy of Fusion. For solids, ΔH_{vap} in eq 1 is referred to the enthalpy of sublimation, which is approximately regarded as the sum of ΔH_{fus} and ΔH_{vap} (liquid to vapor). Table III gives the experimental values of melting point and enthalpy of fusion for crystalline and amorphous β -carotene. The employed crystalline β -carotene was obtained by crystallizing from benzene and methanol. ΔH_{fus} of crystalline β -carotene is larger

than that of amorphous β -carotene. This suggests that the solubility in dense gas of crystalline β -carotene is expected to be lower than that established for amorphous β -carotene.

Glossary

b	constant ($=q - \ln([1000M_B]^k/[M_A + kM_B])$)
ΔH	molar enthalpy, J mol^{-1}
k	association number
M	molecular weight
q	constant in eq 1
R	gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
S	solubility, g m^{-3}
T	temperature, K
y	mole fraction

Greek Letters

ρ	density, kg m^{-3}
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Subscripts

A	solute
B	solvent
fus	fusion
m	melt
solv	solvation
vap	vaporization

Registry No. CO_2 , 124-38-9; N_2O , 10024-97-2; β -carotene, 7235-40-7.

Literature Cited

- (1) Stahl, E.; Schilz, W.; Schutz, E.; Willing, E. *Angew. Chem., Int. Ed. Engl.* **1976**, *17*, 731.
- (2) Eggers, R.; Slevers, U.; Stein, W. *J. Am. Oil Chem. Soc.* **1985**, *62*, 1222.
- (3) King, M. B.; Bott, T. R.; Barr, M. J.; Mahmud, R. S. *Sep. Sci. Technol.* **1987**, *22*, 1103.
- (4) Fattori, M.; Bulley, N. R.; Meisen, A. *J. Am. Oil Chem. Soc.* **1988**, *65*, 968.
- (5) Temelli, F.; O'Connell, J. P.; Chen, C. S.; Braddock, R. J. *Ind. Eng. Chem. Res.* **1990**, *29*, 618.
- (6) Foster, N. R.; Jackson, T.; Chaplin, R. P.; Long, K. K.; Ting, S.; Yun, S. L. *J. Sep. Sci. Technol.* **1991**, *26*, 243.
- (7) Zou, M.; Yu, Z. R.; Kashullines, P.; Rizvi, S. S. H.; Zollweg, J. A. *J. Supercrit. Fluids* **1990**, *3*, 23.
- (8) Cygnarowicz, M. L.; Maxwell, R. J.; Seider, W. D. *Fluid Phase Equilib.* **1990**, *59*, 57.
- (9) Sakaki, K.; Yokochi, T.; Suzuki, O.; Hakuta, T. *J. Am. Oil Chem. Soc.* **1990**, *67*, 553.
- (10) Brunner, G.; Peter, S. *Sep. Sci. Technol.* **1982**, *17*, 199.
- (11) Chrastil, J. *J. Phys. Chem.* **1982**, *86*, 3016.
- (12) Angus, S.; Armstrong, B.; de Reuck, K. M. *International Thermodynamic Tables of the Fluid State. Carbon Dioxide*; Pergamon Press: Oxford, U.K., 1976; Vol. III.
- (13) Couch, E. J.; Kobe, K. A.; Hirth, L. J. *J. Chem. Eng. Data* **1961**, *6*, 229.

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