JOURNAL OF CHEMICAL & ENGINEERING DATA

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Solubilities and Adsorption Equilibria of β-Carotene in Supercritical and Near-Critical Fluids

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ABSTRACT: A systematic investigation of solubility and adsorption equilibria of β-carotene in carbon dioxide and propane, respectively, at elevated pressures was carried out. Investigated at (303, 313, and 323) K and over a pressure range from (3.2 to 13.4) MPa, the solubility of β-carotene in propane was in the range of (110 to 450) $\text{mg} \cdot \text{kg}^{-1}$ propane and approximately 2 orders of magnitude higher than that in supercritical carbon dioxide. Adsorption equilibria of β-carotene in carbon dioxide with a modifier and in propane were studied on nonpolar chromatographic adsorbents. Concerning adsorption equilibria of β-carotene in carbon dioxide with 2-propanol as a modifier, the loading decreases with increasing modifier content and increasing pressure. Regarding the adsorption equilibrium of β-carotene in propane, the loading achieved is much lower than in carbon dioxide due to the higher solubility of β-carotene in propane.

INTRODUCTION

The recovery of high purity products from natural sources has gained more and more interest. To obtain pure substances from natural multicomponent mixtures at a process scale, adsorptive separation provides one possible process. For the operation and development of adsorption processes, especially for multicomponent systems with supercritical solvents like CO_2 or near-critical solvents like propane, the knowledge of thermodynamic data as solubility and adsorption equilibrium is of fundamental importance.[1]

Nicoud and Seidel-Morgenstern published a review about the experimental determination of adsorption isotherms in liquid chromatography.[2] In spite of the increasing importance, the knowledge of adsorption behavior under high pressure is still scarce. Most of the research on adsorption under high pressure is about the adsorption of the pure supercritical fluid. Bamberger showed adsorption equilibria of naphthalene from CO_2 on silica gel; the adsorption of CO_2 on silica gel was also studied.[3] Kikic et al. determined adsorption equilibria of salicylic acid on active carbon.[4] Langmuir and Freundlich isotherms were applied. Cross and Akgerman studied adsorption equilibria of hexachlorobenzene and pentachlorophenol from carbon dioxide on Calcium montmorillonite.[5] Subra et al. investigated adsorption equilibria of a mixture of 13 different terpenes from supercritical CO_2 on silica gel.[6] The solvent was shown to compete for adsorption. Buss studied the adsorption equilibrium of α-tocopherol and vitamin D_3 from CO_2 on cyano-modified silica gel (Zorbax Pro 10-60 CN).[7] The isotherms show anti-Langmuir behavior. Adsorption isotherms of α- and δ-tocopherol on Nucleosil 100-5 and Kromasil KR60-10-SIL were determined.[8,9] The fluid phase was CO_2 with 2-propanol as a modifier. Parameters of a cubic Hill isotherm were fitted to the data. Ideal adsorbed solution (IAS) theory was applied for prediction of mixture adsorption. The adsorption and desorption of lipids on silica gel and Neusilin using supercritical CO_2 as fluid phase were investigated.[10] The adsorption kinetics were determined by analyzing breakthrough curves. Zhou et al. presented a model to predict the adsorption equilibrium of mixtures containing supercritical components.[11] The model was verified by experimental data of the mixture $CH_4/CO_2/C_2H_6$ on activated carbon JX101.

The separation of carotenoids can be achieved using adsorption processes with supercritical fluids like chromatography with supercritical CO_2 as mobile phase.[12] However, due to the low solubility of carotenoids in CO_2, modifiers (cosolvents) such as alcohols are often necessary. The solubilities of important phytonutrients are much higher in propane[13] than in CO_2 so that adsorption processes with propane can be carried out at lower pressure and with less solvent. Besides, the addition of a modifier is unnecessary.

Few solubility data of β-carotene in near- and supercritical CO_2 could be found in the literature as summarized in Table 1.[14−27] Most of the measured solubilities ranged between mole fractions $y = (10^{-6} \text{ to } 10^{-7})$. Most experimental measurements were carried out only up to a pressure of 30 MPa and a temperature of 333 K. Among all of the published data, the maximum solubility obtained was mole fraction $y = 3.24 \cdot 10^{-6}$ at 32 MPa and 353 K, which was obtained from the work of Johannsen and Brunner.[20] The solubility of β-carotene in supercritical fluids and liquefied gases is generally much lower than in organic solvents (typically $(10^{-4} \text{ to } 0.1)\ \text{g} \cdot \text{kg}^{-1}$ compared with $(0.1 \text{ to } 10)\ \text{g} \cdot \text{kg}^{-1}$).[16]

Generally, the solubility increases significantly with the addition of cosolvents in low concentrations. Studies on this aspect were carried out for β-carotene/CO_2/cosolvent systems as listed in Table 2.[14,15,24,26] Ethanol was considered as the most common used cosolvent and investigated by all authors who studied the enhancement effect on solubility of β-carotene by addition of cosolvent. Other solvents that were tested as cosolvent include methanol, methylene chloride, acetone, vegetable oil, acetic acid,

Received: June 3, 2010
Accepted: February 1, 2011
Published: February 25, 2011

dx.doi.org/10.1021/je100229f | J. Chem. Eng. Data 2011, 56, 1770–1777

and hexane. Among the solubility data obtained from the studies listed in Table 2, Cygnarowicz et al. reported the highest solubility value of β-carotene by using ethanol (mass fraction $w = 0.01$) as cosolvent, which was $3.8 \cdot 10^{-6}$.[14]

Differences between β-carotene solubility in different sub/supercritical fluids are due to molecular properties of the solvent such as the dipole moment μ and molecular polarizability. Besides CO_2 ($T_c = 304.2$ K, $p_c = 7.38$ MPa, $\mu = 0.0$ Cm), some other available gases having critical points close to room temperature were tested as solvents for β-carotene: N_2O, SF_6, CHF_3, $CClF_3$, C_2H_6, and C_2H_4, as summarized in Table 3.[16,17,19,21,25,28−30] Jay and Steyler studied the solubility of β-carotene in various supercritical fluids.[16] They reported that highest solubility was obtained at 313 K with N_2O (mole fraction $y = 5.9 \cdot 10^{-6}$) and at 328 K with C_2H_4 (mole fraction $y = 8.3 \cdot 10^{-6}$), both at 50 MPa. Jay and Steyler and Chang and Randolph both agreed that C_2H_4 is a moderately good supercritical solvent for β-carotene.[16,28] Sakaki also reported that N_2O is a better solvent for β-carotene than CO_2.[17] Mendes et al. reported that ethane was a better supercritical solvent than CO_2 by about 1 order of magnitude.[21] The solubility value obtained from Jay and Steytler, however, is the only existing solubility data of β-carotene in near-critical propane ($T_c = 369.8$ K, $p_c = 4.25$ MPa, $\mu = 0.0$ Cm) found in the literature.[16] The solubility value obtained from their work is mole fraction $y = 6.6 \cdot 10^{-6}$, which is equivalent to 79 $\text{mg} \cdot \text{kg}^{-1}$ at a pressure of 0.73 MPa and temperature of 298 K.

All of the studies listed in Table 3 dealt with single-solvent systems. To date, only Nobre et al. investigated the solubility of β-carotene in near-critical mixtures (ethane (1) + propane (2)).[29] Two mixtures containing propane mole fractions of $x_2 = 0.5$ and $x_2 = 0.6$, respectively, were tested. The maximum

Table 1. Synopsis of Solubility Measurements of β-Carotene in Supercritical Carbon Dioxide in the Literature

p/MPa	T/K	author(s)
20.0−45.0	313−343	Cygnarowicz et al. (1990)[14]
5.0−80.0	288−328	Jay et al. (1991)[15]
5.0−50.0	288−328	Jay and Steytler (1992)[16]
10.0−30.0	308−323	Sakaki (1992)[17]
10.0−30.0	298−313	Skerget et al. (1995)[18]
9.0−28.0	310−340	Subra et al. (1997)[19]
20.0−32.0	313−353	Johannsen and Brunner (1997)[20]
12.0−30.0	313−333	Mendes et al. (1999)[21]
30.0	313−333	Cocero et al. (2000)[22]
6.0−35.0	313−333	Hansen et al. (2001)[23]
12.0−28.0	313−333	Sovova et al. (2001)[24]
80.0−180.0	308−323	Kraska et al. (2002)[25]
15.0−28.0	313−333	Huang et al. (2006)[26]
12.0−20.0	313−323	Saldaña et al. (2006)[27]

Table 2. Synopsis of Solubility Measurements of β-Carotene in Supercritical Carbon Dioxide with Cosolvents in the Literature

cosolvent	cosolvent mass fraction w	p/MPa	T/K	author(s)
methanol	0.01	18.0−38.0	343	Cygnarowicz et al. (1990)[14]
ethanol	0.01	18.0−38.0	343	
dichloromethane	0.01	18.0−38.0	343	
ethanol	0.05	5.0−80.0	288−328	Jay et al. (1991)[15]
acetone	0.05	5.0−80.0	288−328	
acetic acid	0.01	5.0−80.0	288−328	
ethanol	0.003−0.024	12.0−28.0	313−333	Sovova et al. (2001)[24]
vegetable oil	0.0015−0.0067	12.0−28.0	313−333	
ethanol	0.05, 0.1	15.0−28.0	313−333	Huang et al. (2006)[26]
acetone	0.05, 0.1	15.0−28.0	313−333	
hexane	0.05, 0.1	15.0−28.0	313−333	

Table 3. Synopsis of Solubility Measurements of β-Carotene in Other Near-Critical Solvents in the Literature

solvent	p/MPa	T/K	author(s)
C_2H_4	10.0−37.0	323−343	Chang and Randolph (1989)[28]
C_2H_4 + toluene	31.0−37.0	343	
N_2O	5.0−50.0	288−313	Jay and Steytler (1992)[16]
C_2H_6	3.0−35.0	288−328	
C_2H_4	20.0− 50.0	308−328	
Xe	11.0−30.0	300−329	
SF_6	35.0	323	
C_3H_8, $CHClF_2$, NH_3, SO_2, CCl_2F_2	<1.0	288	
N_2O	10.0−30.0	308−323	Sakaki (1992)[17]
N_2O	9.0−28.0	310−340	Subra et al. (1997)[19]
C_2H_6	9.0−25.0	308−333	Mendes et al. (1999)[21]
N_2O	12.0−28.0	308−323	Tuma and Schneider (1999)[29]
$CClF_3$	25.0−180.0	296−326	Kraska et al. (2002)[25]
C_3H_8 + C_2H_6	5.0−30.0	313 - 348	Nobre et al. (2002)[30]

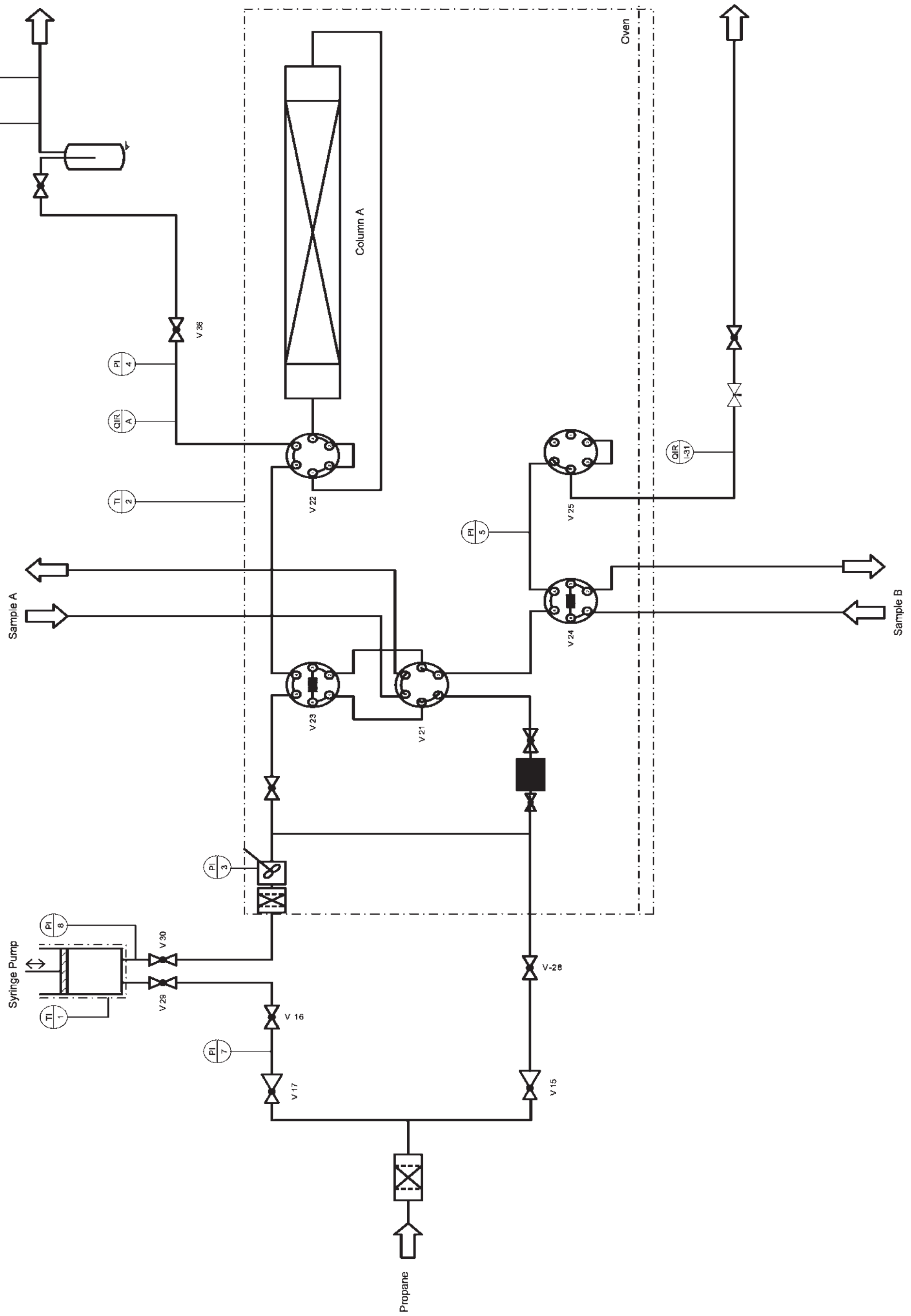

Figure 1. Flow sheet of the experimental setup for solubility measurements.

solubility concentration obtained through that work was 1 order of magnitude higher than in single-solvent systems. The solubility obtained were in the range of mole fraction $y = (0.4 \cdot 10^{-6}$ to $9.4 \cdot 10^{-5})$ for $x_2 = 0.5$ and $y = (5.1 \cdot 10^{-6}$ to $9.2 \cdot 10^{-5})$ for $x_2 = 0.6$.

In this work, the solubility and adsorption of β-carotene from supercritical CO_2 or liquid propane will be presented. The influence of various factors such as type of adsorbents, composition of solvent (desorbent), temperature, and pressure will be studied. The results will be modeled with known isotherm models. These models can be applied for example for the simulation of chromatographic processes to ease the choices of suitable process parameter.

■ EXPERIMENTAL SECTION

Materials. Carbon dioxide was supplied by YARA Industrial (Bad Hönnigen, Germany). The purity of CO_2 is more than 99.95 mass %. Propane, C_3H_8 (≥ 99.5 mass %), supplied by Westfalen AG was used. β-Carotene, $C_{40}H_{56}$ (≥ 97 mass %), was supplied by Fluka (Germany) and stored under N_2 at 255 K. 2-Propanol was used as a modifier. It has a manufacturing purity of 99 mass % (GC analysis) and was obtained from BASF (Ludwigshafen, Germany). Cyclohexane, C_6H_{12} (≥ 99 mass %), was obtained from Merck (Darmstadt, Germany). It was used as solvent to dissolve β-carotene for sample injections. Tetrahydrofuran (C_4H_8O), obtained from Fluka (Germany), was also used as solvent for β-carotene for the determination of the adsorption isotherms. It has a purity of ≥ 99.8 mass % (GC analysis).

The modified silica gel, Nucleosil 100-5-C_{18} produced by Macherey-Nagel (Germany), has spherical particles with a diameter of 5 μm and pore size of 10 nm. It has a packed density of 0.36 $g \cdot mL^{-1}$ and surface area of 350 $m^2 \cdot g^{-1}$. It was used as stationary phase and prepacked in a chromatographic column (250 × 4.6 mm) for the experiments with CO_2 as the solvent.

Kromasil RP C_{18} (5 μm) kindly donated by Eka Chemicals (Sweden) was applied as the stationary phase. It has spherical particles with a diameter of 5 μm and pore size of 10 nm. It has a packed density of 0.66 $g \cdot mL^{-1}$ and surface area of 320 $m^2 \cdot g^{-1}$. It was delivered as bulk material, packed in a chromatographic column (250 × 4.6 mm), and used for the determination of adsorption isotherm with propane as solvent.

Apparatus. The experimental setup that was used for measurement of adsorption equilibria was presented before.[9] To measure the solubility of β-carotene in propane by a static analytical method with direct coupling of an equilibrium cell, the supercritical fluid setup was modified. The alternative configuration is shown in Figure 1. The solvent is prepared and brought to operating pressure with a modified fluid compression module (PM-101, NWA, Lörrach/Germany). It is passed through a 0.5 μm sintered metal filter to avoid any impurities. For solubility measurements an equilibrium cell was necessary to be installed in the oven (between the valves V21 and V28). For this purpose a stainless steel high-performance liquid chromatography (HPLC) column (125 mm length × 4 mm inner diameter (i.d.)) equipped with frits (2 μm) at both ends was used. This 4 mL equilibrium cell was loaded with a sufficient amount of the β-carotene and some glass beads for sample mixing. Glass wool was filled at both ends of the cell to retain the solid in equilibrium cell. The pressure was measured with an uncertainty of ± 0.1 MPa with a pressure gauge mounted at the outlet of the pump. The columns and valves are located in an oven (WTB FED 53, Binder, Tuttlingen/Germany) where solvent is brought to the operating temperature with an uncertainty of ± 1 K. For each measurement, sufficient time is required to allow the system to reach equilibrium. According to the preliminary experiments, it is found that around 30 min was required for the equilibration time.[20] Samples were taken by a six-port valve (V23) equipped with a 5 μL sample loop and analyzed on a HPLC-type packed column (column A) of 125 mm length × 4 mm i.d., packed with 5 μm particles of Kromasil RP C_{18}. To ensure a continuous and steady fluid flow to column A, the solvent is transported through the system with the help of a syringe pump (ISCO 260D, Lincoln/USA) during the process. After passing the analytical column, the solvent flows through a DAD detector (Smartline 2600, Knauer GmbH, Berlin/Germany), for determination of the concentration. The signals from the detectors and the experimental data are recorded by using a chromatographic software (EUROCHROM, Knauer GmbH, Berlin/Germany). Expansion of the fluid after detection was controlled by an expansion module (PE-103, NWA, Lörrach/Germany), and the gas flow rate at atmospheric pressure is measured.

For adsorption measurements there are two possible modes for operating the experimental setup as presented before.[8,9] One is the injection mode and the other the perturbation mode that can be attained by switching the positions of the transfer valve V21. In this work the injection mode was used. Column A was filled with the adsorbent to be investigated, and line A of the experimental setup for measurement of adsorption equilibria is used only. The samples are injected into the corresponding loops with a syringe. The volumes of the injection loop can be varied.

Calibration. For the detector calibration, a relationship between the injected mass m_{inj} and an integral of the resulted peak is used:

$$m_{\text{inj}} = V \cdot \int_0^\infty c(t)\, dt \tag{1}$$

with volume flow rate V, concentration in the fluid phase c, and time t. When analyzing overloaded peaks, the concentration to be taken into account must be as high as possible, and this is mostly done by a nonlinear equation. To make a simple adjustment of the parameters, cubic polynomials are considered to be suitable:

$$c = e_1 D + e_2 D^2 + e_3 D^3 \tag{2}$$

with fitting parameters e_1, e_2, and e_3 and detector signal D. For the optimization of the parameters, many chromatograms have to be evaluated, and eq 3 is derived.

$$\sum_n [m_n^{\text{inj}} - V_n(e_1 \int_0^\infty D_n\, dt + e_2 \int_0^\infty D_n^2\, dt + e_3 \int_0^\infty D_n^3\, dt)]^2 = \min \tag{3}$$

For the calibration of the detector, an injection loop of 20 μL was used, and a concentration of (0.75, 1.0, and 1.5) $mg \cdot mL^{-1}$ of β-carotene in cyclohexane was injected. The average pressure and the temperature of the column were 20 MPa and 313 K, respectively. The 10 samples of each concentration cited above were injected into the loop. The peaks were analyzed, and the parameters e_1, e_2, and e_3 were obtained ($r^2 = 0.99$):

$$c = 1.27 \cdot 10^{-5} \cdot D + 2.35 \cdot 10^{-9} \cdot D^2 - 3.28 \cdot 10^{-12} \cdot D^3 \tag{4}$$

RESULTS AND DISCUSSION

Determination of Solubility. The solubilities of β-carotene in near-critical propane were determined at (303, 313, and 323) K and over the range of pressure from (3.2 to 13.4) MPa. The results of solubility measurements of β-carotene in propane are presented in Table 4 and in Figure 2. Solubility data presented are the mean value of at least four samplings. The densities of the near-critical propane were obtained with the software ThermoFluids using the Bücker−Wagner equation of state (EOS)[30] and listed in Table 4. It can be seen from Figure 2 that the solubility increases with pressure as well as temperature. Within the ranges of pressure and temperature investigated, the solubilities of β-carotene in propane obtained in this work ranged from $0.9 \cdot 10^{-5}$ (113 $mg \cdot kg^{-1}$) at 303 K and 3.25 MPa to $3.6 \cdot 10^{-5}$ (442 $mg \cdot kg^{-1}$) at 323 K and 12.2 MPa.

The solubility was determined at three temperatures. The difference between solubility isotherms at (303 and 323) K is approximately a factor of about 2 to 2.5, depending on vapor pressure of the solute and density of the fluid. Increasing vapor pressure compensates the decrease in density by increasing temperature. For example at 3.2 MPa, the solvent density decreases from 492 $kg \cdot m^{-3}$ at 303 K to 457 $kg \cdot m^{-3}$ at 323 K. However, the vapor pressure of solute is increasing with increasing temperature. Thus, the solubility of β-carotene is increasing from mole fraction $y = 0.9 \cdot 10^{-5}$ to $y = 1.6 \cdot 10^{-5}$.

Table 4. Solubilities (S, y) of β-Carotene in Near-Critical Propane at (313, 323, and 333) K

T	p	ρ	S	
K	MPa	$\mathrm{kg \cdot m^{-3}}$	$\mathrm{mg \cdot kg^{-1}}$	$y/10^{-5}$
303 ± 1	3.25 ± 0.1	491.7 ± 2.2	112.6 ± 1.7	0.92 ± 0.01
	5.4 ± 0.1	497.8 ± 1.7	125.6 ± 4.9	1.03 ± 0.04
	6.3 ± 0.1	500.1 ± 1.6	127.7 ± 0.9	1.05 ± 0.01
	7.4 ± 0.1	502.9 ± 1.6	136.6 ± 2.4	1.12 ± 0.02
	8.8 ± 0.1	506.2 ± 1.5	147.4 ± 1.9	1.21 ± 0.02
	9.65 ± 0.1	508.1 ± 1.5	151.5 ± 3.5	1.24 ± 0.03
	11.0 ± 0.1	511.0 ± 1.5	171.4 ± 5.2	1.41 ± 0.04
	12.7 ± 0.1	514.5 ± 1.4	204.5 ± 2.1	1.68 ± 0.02
313 ± 1	3.2 ± 0.1	475.2 ± 2.1	138.9 ± 1.7	1.14 ± 0.01
	4.65 ± 0.1	480.3 ± 1.9	157.8	1.30
	6.9 ± 0.1	487.3 ± 1.8	182.7 ± 8.6	1.50 ± 0.07
	8.0 ± 0.1	490.4 ± 1.7	201.0 ± 7.8	1.65 ± 0.06
	9.2 ± 0.1	493.7 ± 1.6	221.8 ± 6.9	1.82 ± 0.06
	10.2 ± 0.1	496.2 ± 1.6	236.2 ± 4.6	1.94 ± 0.04
	12.0 ± 0.1	500.5 ± 1.5	246.0 ± 4.2	2.02 ± 0.03
	13.4 ± 0.1	503.7 ± 1.4	276.4 ± 1.3	2.27 ± 0.01
323 ± 1	3.2 ± 0.1	457.0 ± 2.4	194.9 ± 2.3	1.60 ± 0.02
	4.8 ± 0.1	464.1 ± 2.1	227.5 ± 6.3	1.87 ± 0.05
	7.3 ± 0.1	473.4 ± 1.9	297.1 ± 5.9	2.44 ± 0.05
	8.6 ± 0.1	477.7 ± 1.8	331.8 ± 15.9	2.73 ± 0.13
	10.6 ± 0.1	483.6 ± 1.6	377.7 ± 5.9	3.10 ± 0.05
	12.2 ± 0.1	488.0 ± 1.6	441.8 ± 5.3	3.63 ± 0.04

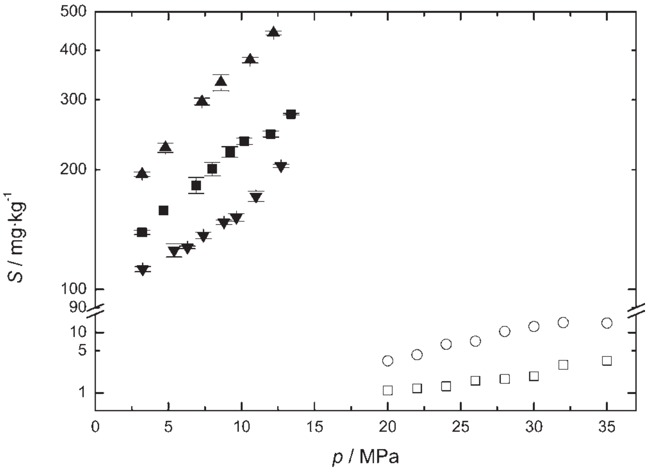

Figure 2. Comparison of solubilities S of β-carotene in propane (this work): ▲, T = 323 K; ■, T = 313 K; ▼, T = 303 K; and in CO_2 (ref 20): ○, T = 333 K; □, T = 313 K.

A comparison is made between the solubility in propane and in carbon dioxide.[20] Although both fluids are nonpolar, propane has a higher molecular polarizability than CO_2 ($6.3 \cdot 10^{-24}$ and $2.9 \cdot 10^{-24}$ $\mathrm{cm^3}$, respectively).[16,19] From Figure 2 it can clearly be seen that the solubility of β-carotene in propane is about 2 orders of magnitude higher than the one in CO_2. Around (100 to 450) mg of β-carotene dissolved in 1 kg of propane, whereas with CO_2, only 15 mg of β-carotene is dissolved in 1 kg of CO_2. As can be seen also, relatively low pressures are needed to carry out a separation process by using propane.

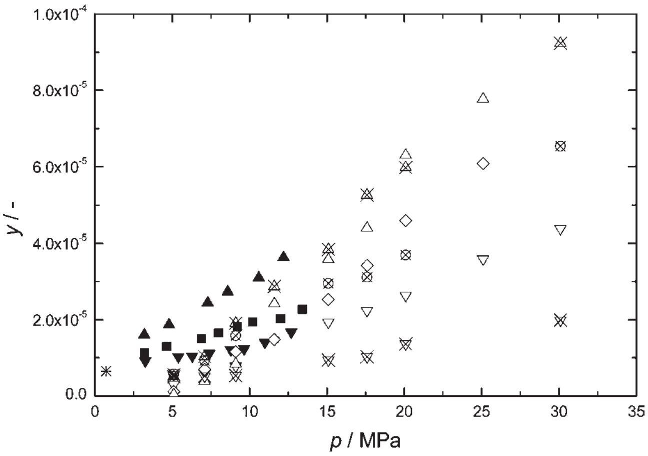

Figure 3. Comparison of solubilities of β-carotene in pure propane (1) and in mixtures of propane (1) and ethane (2). This work ($x_1 = 1$): ▲, T = 323 K; ■, T = 313 K; ▼, T = 303 K. Jay and Steytler[16] ($x_1 = 1$): ∗, T = 323 K. Nobre et al.[29] ($x_1 = x_2 = 0.5$): △, T = 348 K; ◇, T = 343 K; ▽, T = 333 K. Nobre et al.[29] ($x_1 = 0.6$ and $x_2 = 0.4$): △ with ×, T = 343 K; ⊗, T = 333 K; ▽ with ×, T = 313 K.

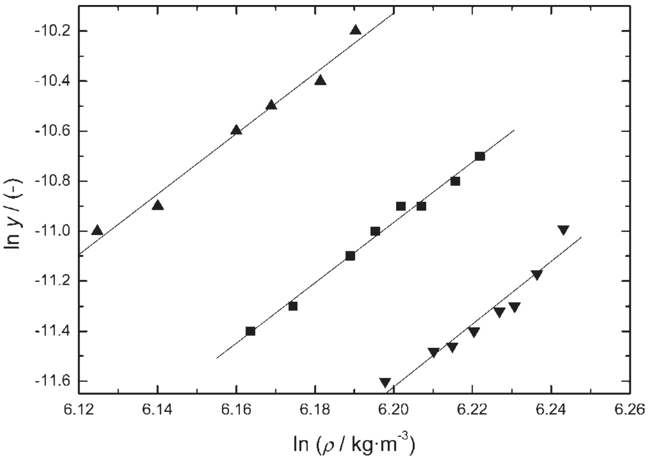

Figure 4. Correlation using the Chrastil model of measured solubilities of β-carotene in propane: ▲, T = 323 K; ■, T = 313 K; ▼, T = 303 K.

Besides carbon dioxide, ethane and propane also can be applied under sub- and supercritical conditions. Their critical temperature and pressure are easy to reach, and they are nontoxic, noncorrosive, and extremely stable. One single solubility value of β-carotene in propane was reported by Jay and Steytler.[16] They measured at wavelength of 441 nm, at pressure of 0.73 MPa, and temperature of 288 K. The solubility value obtained was 79 $\mathrm{mg \cdot kg^{-1}}$ (mole fraction $y = 6.5 \cdot 10^{-6}$). Nobre et al. measured the solubility of β-carotene in mixtures of ethane and propane.[31] Using solvent mixtures is advantageous, as it can simultaneously increase the solvent power and maintain the operation temperature of the supercritical systems below the value at which degradation of the β-carotene occurs. It was found that solubility increased with the amount of propane in the mixture. This is due to the higher molecular polarizability of propane than ethane ($6.3 \cdot 10^{-24}$ $\mathrm{cm^3}$ and $4.4 \cdot 10^{-24}$ $\mathrm{cm^3}$, respectively).[31] As observed from the Figure 3, it is found that, by using pure propane, the solubility value is higher even though at lower pressure and lower temperature.

Table 5. Conditions for the Measurements of Adsorption Isotherms in CO_2 and Propane

desorbent	CO_2	propane
adsorbent	Nucleosil C_{18}	Kromasil RP C_{18}
concentration of injected solution	(0.5, 1.0, 1.75, 3.5, 5.25, 7.0) $mg \cdot mL^{-1}$	(0.25, 0.5, 0.75, 1.0) $mg \cdot mL^{-1}$
solvent of samples injected	cyclohexane + THF	cyclohexane
injection loop volume	20 μL	5 μL
inlet pressure of the column	(21.0, 27.0) MPa	2.0 MPa
outlet pressure of the column	(19.0, 23.0) MPa	1.0 MPa
oven temperature	313 K	293 K
modifier (2-propanol) mass fraction	0.04, 0.05, 0.07	-
flow rate	2 $mL \cdot min^{-1}$	1 $mL \cdot min^{-1}$

Modeling the experimental solubility data of β-carotene with Redlich−Kwong−ASPEN EOS did not show satisfactorily correlation. It is apparent that the solubility−density log−log relationship is linear as shown in Figure 4. Therefore, modeling the experimental solubility data of β-carotene in near-critical propane using the density based correlation as proposed by Chrastil is applied:[32]

$$S = \rho^k \exp\left(\frac{a}{T} + b\right) \qquad (5)$$

In this equation, S ($kg \cdot m^{-3}$) is the solubility of the solute in the supercritical phase, ρ ($kg \cdot m^{-3}$), the density of the pure supercritical fluid, k the association number, a (K) a parameter, defined as $\Delta H/R$ (where ΔH is the sum of the enthalpies of vaporization and solvation of the solute and R the gas constant), and b is another parameter related to the molecular weight of the solute and solvent. A comparison between different semiempirical equations (Chrastil and several others) to predict the solubility in supercritical carbon dioxide was published recently.[33] It was found that semiempirical equations present a more accurate prediction compared to cubic equations of state and present no drawbacks such as properties estimation and computational difficulties.

The fitted values of parameters are $k = 12.08$, $a = -6741.9$ K, and $b = -64.15$. The measured solubility data for β-carotene for all temperatures investigated agree well with the Chrastil correlation. The standard deviation was found to be 2.3 %.

Determination of Adsorption Isotherms. The adsorption behavior of β-carotene was studied with the peak maximum method.[2] The experimental data were fitted to the linear adsorption model (eq 6). From the retention time t_R, the linear adsorption coefficient K^H is calculated (eq 7).

$$q = K^H c \qquad (6)$$

where

$$K^H = \frac{dq}{dc} = \frac{\frac{t_R}{t_M} - 1}{F} \qquad (7)$$

with holdup time t_M and phase ratio F.

A linear adsorption isotherm was considered for the sample injections with low concentrations ((0.5 and 1.0) $mg \cdot mL^{-1}$) in cyclohexane as well as with higher concentrations ((1.0, 1.75, 3.5, 5.25, and 7.0) $mg \cdot mL^{-1}$) in tetrahydrofuran. Still higher concentrations could not be used, as solubility of β-carotene in these solvents is limited.

In Table 5 the conditions for the measurements of adsorption isotherms on Nucleosil C_{18} in CO_2 are listed, and in Figure 5 the resulted adsorption isotherms of β-carotene (C_6H_{12}) at (20 and 25) MPa are shown. For both pressures the loading decreases with an increase in modifier content. At higher pressure the loading is lower because of the higher solubility at higher pressure. The obtained experimental data fit well to linear adsorption isotherms.

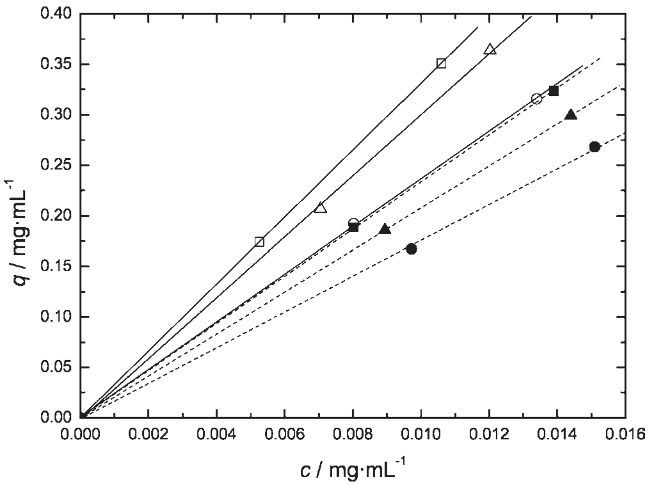

Figure 5. Adsorption isotherm of β-carotene (C_6H_{12}) on Nucleosil RP18 from CO_2 (1) with 2-propanol (2) at $T = 313$ K and $p = 20$ MPa: □, $w_2 = 0.04$; △, $w_2 = 0.05$; ○, $w_2 = 0.07$; and at $T = 313$ K and $p = 25$ MPa: ■, $w_2 = 0.04$; ▲, $w_2 = 0.05$; ●, $w_2 = 0.07$.

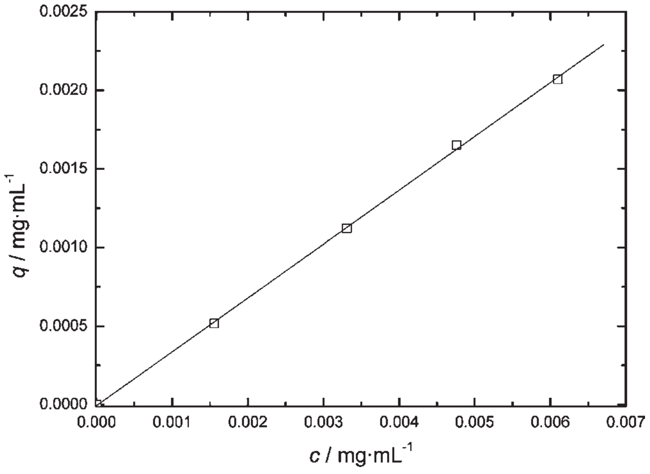

Figure 6. Adsorption isotherm of β-carotene (C_6H_{12}) on Kromasil RP18 from propane at $T = 293$ K and $p = 1.5$ MPa.

Table 6. Linear Adsorption Coefficients K_H of β-Carotene on Nucleosil C_{18} from CO_2 + 2-Propanol and on Kromasil RP C_{18} from Propane

solvent	modifier mass fraction w_2	T/K	p/MPa	K_H
CO_2 (1) + 2-propanol (2)	0.04 ± 0.01	313 ± 1	20.0 ± 0.1	33.1 ± 0.1
CO_2 (1) + 2-propanol (2)	0.05 ± 0.01	313 ± 1	20.0 ± 0.1	29.8 ± 0.4
CO_2 (1) + 2-propanol (2)	0.07 ± 0.01	313 ± 1	20.0 ± 0.1	23.7 ± 0.3
CO_2 (1) + 2-propanol (2)	0.04 ± 0.01	313 ± 1	25.0 ± 0.1	23.4 ± 0.1
CO_2 (1) + 2-propanol (2)	0.05 ± 0.01	313 ± 1	25.0 ± 0.1	20.8 ± 0.1
CO_2 (1) + 2-propanol (2)	0.07 ± 0.01	313 ± 1	25.0 ± 0.1	17.5 ± 0.3
propane	0	293 ± 1	1.5 ± 0.1	0.34 ± 0.01

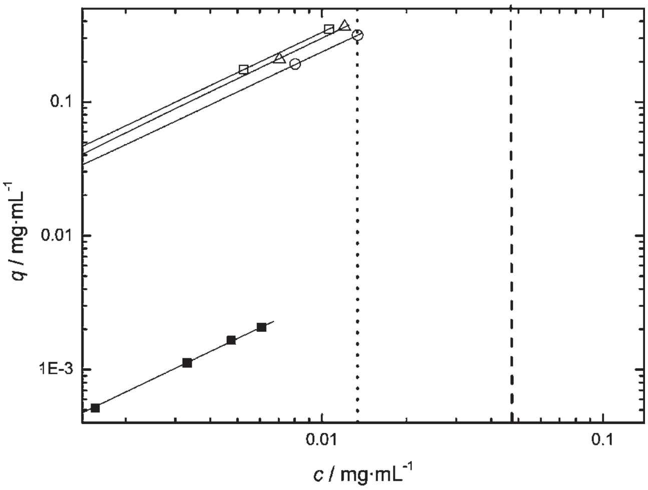

Figure 7. Comparison of adsorption isotherm of β-carotene (C_6H_{12}) on Kromasil RP18 from propane at T = 293 K and p = 1.5 MPa: ■, propane; and on Nucleosil RP18 from CO_2 with modifier 2-propanol (2) at T = 313 K and p = 20 MPa: □, w_2 = 0.04; △, w_2 = 0.05; ○, w_2 = 0.07. Dotted line: c^{sat}(CO_2 with 1 % ethanol) at p = 28 MPa and T = 333 K[24] and dashed line: c^{sat}(propane) at p = 3.3 MPa and T = 303 K.

Table 5 also shows the parameters for the measurement of adsorption isotherms on Kromasil C_{18} in propane. Due to the high solubility of β-carotene in propane, the adsorbent loading is very low. The experimental data fit well with the linear adsorption isotherm as shown in Figure 6. In Table 6 the linear adsorption coefficients calculated from the measurements in CO_2 + 2-propanol and propane are given.

In Figure 7 the adsorption isotherms obtained with propane and CO_2 as solvent are compared. A significant difference in loading between CO_2 and propane as solvent is found. The dotted line represents the solubility of β-carotene in CO_2 at 28 MPa and 333 K with mass fraction w = 0.01 ethanol as cosolvent.[24] The dashed line represents the solubility of β-carotene in propane at 3.3 MPa and 303 K determined in this work. It is expected that the adsorption isotherm will follow a linear trend until it hits the solubility limit. A trend of decreasing loading with increasing solubility in the solvent can be observed. Thus, the loading could be increased with the lowered solubility of β-carotene in solvent. This could be the case if a mixture of propane/CO_2 instead of pure propane is used as solvent. On the other side, this results in a lower saturation concentration in the fluid phase and would set a limit to the adsorbent loading. In other words, a compromise must be met between solubility and loading. Another way to achieve higher loadings would be the application of a different adsorbent, such as bleaching earth or synthetic polymer resins.

CONCLUSIONS

In this work solubility and adsorption equilibria of β-carotene in supercritical carbon dioxide and near-critical propane, respectively, at elevated pressures were investigated. These data are of fundamental importance for the design and modeling of adsorption and chromatographic processes in supercritical fluid phases. Regarding adsorption equilibria of β-carotene in propane on nonpolar adsorbent, the loading achieved is much lower than in carbon dioxide due to the higher solubility of β-carotene in propane. However, the concentrations achieved in the fluid phase are still in the linear range of the adsorption isotherms. In further studies a wider range of concentrations of β-carotene will be investigated to determine adsorption equilibria in nonlinear range if they exist. Other adsorbents, such as bentonite, can be used, since they show a much higher loading for carotenoids than silica gel.[34]

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Funding Sources

Financial support of this work by the German Research Foundation (DFG Grant Jo 339/6) is gratefully acknowledged.

ACKNOWLEDGMENT

The assistance of Arun K. Macha and Wai Keng Teng is gratefully acknowledged.

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