Solubilities of the Fat-Soluble Vitamins A, D, E, and K in Supercritical Carbon Dioxide

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Solubilities of eight different species of the fat-soluble vitamins A, D, E, and K in supercritical carbon dioxide were measured at (313, 333, and 353) K and over a pressure range of 20 MPa to 35 MPa. Solubilities have been determined by an analytical method using the direct coupling of an equilibrium cell to a supercritical fluid chromatographic system with UV detection. The solubilities of all fat-soluble vitamins in supercritical carbon dioxide under the conditions investigated are in the range of 10 g/kg, except for β-carotene (provitamin A), which is 3 orders of magnitude less soluble. With increasing molecular mass of the vitamin, its solubility in supercritical carbon dioxide decreases. At constant temperature, the solubility of all substances increases with increasing density. At constant density, a rise of temperature results in an increase in solubility. This is caused by the increasing vapor pressure of the solid.

Introduction

During the last 30 years the interest in the technical use of supercritical fluids has increased. There are important applications in the field of extraction, chromatography, and reactions using supercritical fluids.

Supercritical fluid extraction (SFE) makes possible a selective and mild isolation of substances from natural material. Some of the most well-known applications of technical gas extraction are the decaffeination of coffee and tea, and the extraction of hops, spices, drugs, and natural colors with supercritical carbon dioxide. There has also been a growing interest in preparative supercritical fluid chromatography (SFC), which shows the same advantages as technical SFE (Brunner, 1994). In addition the selectivity of a chromatographic separation could be influenced substantially by choosing the most suitable stationary phase adsorbent material. The use of supercritical fluids as solvents leads to a reduction or elimination of organic and partly chlorinated solvents in all these areas.

The knowledge of the characteristic phase equilibrium is of considerable economic interest for optimal calculation of separation processes controlled by phase equilibrium. Separation costs may comprise up to 80% of the total investment and running costs of a production process.

In this work, the solubility data of the fat-soluble vitamins A, D, E, and K are presented. Presently fat-soluble vitamins are mainly produced synthetically. However, their isolation from natural sources is of increasing interest. Only a few solubility data of tocopherols (vitamin E) and β-carotene (provitamin A) in supercritical fluids have been published. These data are listed in Tables 1 and 2.

Experimental Section

Apparatus and Procedure. An apparatus for the quasi-static measurement of equilibrium solubilities with on-line coupling to a supercritical fluid chromatographic system was used. This apparatus and the procedure have been described before (Johannsen and Brunner, 1994a,b, 1996).

Table 1. Synopsis of Solubility Measurements of Tocopherols in Supercritical CO_2 in the Literature

tocopherol	P/MPa	T/K	author(s)
α	8−20	313−353	Chrastil (1982)
α	10−18	298, 313	Ohgaki et al. (1989)
α	15−35	327−353	Zehnder (1992)
α	10−35	303−353	Meier (1992); Meier et al. (1994)
α	9−26	292−333	Pereira et al. (1993)
α, δ	9−26	313	Pereira et al. (1994); Pereira (1995)
α	7−35	313−353	Birtigh et al. (1995)
α	10−20	313−333	Schaffner and Trepp (1995)

Materials. Carbon dioxide of 99.95 mass % purity was from KWD, Kohlensäurewerke Deutschland, Bad Hönningen, Germany. Carbon dioxide was fed to the system from the vapor phase of a carbon dioxide tank, further dried by a moisture trap containing a molecular sieve, and liquefied in the cylinder. The vitamins were obtained from various sources, as shown in Table 3.

Results and Discussion

The solubilities of eight different species of the fat-soluble vitamins A, D, E, and K in supercritical carbon dioxide were measured at temperatures of (313, 333, and 353) K and over a pressure range of (20 to 35) MPa. The experimental results are reported in Tables 4−11. The pressure was measured to an accuracy of ±0.1 MPa, and the temperature regulation was within ± 1 K. Densities of pure CO_2 were calculated with the Bender equation of state (Bender, 1970). All solubility values represent mean values of at least five samplings. Standard deviations of the measurements were within 5%. In what follows some selected results are considered.

In Figure 1, the solubilities of α- and δ-tocopherol (2) in supercritical carbon dioxide (1) are presented as a function of the CO_2 density in a semilogarithmic scale. The solubilities of tocopherols measured under these conditions are in the range of (5 to 40) g/kg, corresponding to $x_2 = (0.5 \times 10^{-3}$ to $4.6 \times 10^{-3})$. There are no remarkable differences between the solubilities of α- and δ-tocopherol. For both isomers the lowest solubility was found at a temperature of 353 K and a pressure of 20 MPa (density about 590 kg/m^3) and the highest one at a temperature of 333 K and a pressure of 35 MPa (density about 860 kg/m^3).

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S0021-9568(96)00219-1 CCC: $14.00

Table 2. Synopsis of Solubility Measurements of *β*-Carotene in Supercritical Fluids in the Literature

solvent	*P*/MPa	*T*/K	author(s)
CO_2	20−50	313−343	Cygnarowicz et al. (1990)
CO_2, N_2O	9.6−30	308−323	Sakaki (1992)
CO_2, N_2O, C_2H_4, Xe, SF_6, C_3H_8, etc.	0.15−50 (single data)	288−329 (single data)	Jay and Steytler (1992)
CO_2	10−30	298−313	Skerget et al. (1995)

Table 3. Purities and Manufacturer of the Test Compounds

compound	purity/%	manufacturer (all in Germany)	product no.
trans-retinol (vitamin A)	approx 70	Sigma, Deisenhofen	R 7632
trans-*β*-carotene	approx 95	Sigma, Deisenhofen	C 9750
vitamin E (DL-α-tocopherol)	>98	Fluka, Neu-Ulm	95240
δ-tocopherol	approx 90	Sigma, Deisenhofen	T 2028
vitamin D_2 (ergocalciferol)	97−100	Merck, Darmstadt	8533
vitamin D_3 (cholecalciferol)	97−100	Merck, Darmstadt	8523
vitamin K_1	>99	Merck, Darmstadt	8355
vitamin K_3 (menadione)	>98	Sigma, Deisenhofen	M 5625

Table 4. Solubility *S* (in Grams per Kilogram of Solvent) and Mole Fraction Solubility x_2 of α-Tocopherol (2) in Supercritical Carbon Dioxide (1)

T/K	*P*/MPa	ρ/kg·m^{-3}	*S*/g·kg^{-1}	$x_2/10^{-3}$
313	19.9	839.3	13.7	1.42
	21.9	856.8	16.3	1.69
	23.9	872.3	18.1	1.88
	25.9	886.1	20.2	2.10
	27.9	898.5	23.6	2.46
	29.9	909.9	25.5	2.67
	31.9	920.5	25.7	2.69
	34.9	935.0	27.7	2.90
333	19.9	721.6	10.6	1.09
	21.9	750.8	13.6	1.41
	23.9	774.9	17.1	1.77
	25.9	795.4	19.8	2.06
	27.9	813.3	22.9	2.39
	29.9	829.2	25.1	2.62
	31.9	843.5	29.4	3.09
	34.9	862.7	33.9	3.57
353	19.9	591.6	6.2	0.64
	21.9	634.9	10.1	1.04
	23.9	669.7	14.4	1.49
	25.9	698.6	17.3	1.80
	27.9	723.2	19.9	2.07
	29.9	744.5	23.1	2.41
	31.9	763.4	28.4	2.98
	34.9	788.2	33.2	3.50

Table 5. Solubility *S* (in Grams per Kilogram of Solvent) and Mole Fraction Solubility x_2 of *δ*-Tocopherol (2) in Supercritical Carbon Dioxide (1)

T/K	*P*/MPa	ρ/kg·m^{-3}	*S*/g·kg^{-1}	$x_2/10^{-3}$
313	19.9	840.2	9.7	1.08
	21.9	857.7	10.4	1.15
	23.9	873.0	11.7	1.30
	25.9	886.7	15.1	1.68
	27.9	899.1	21.2	2.37
	29.9	911.0	25.0	2.79
	31.9	921.0	27.3	3.06
	34.9	935.9	30.8	3.46
333	19.9	723.2	7.9	0.87
	21.9	753.4	11.7	1.29
	23.9	778.2	17.5	1.95
	25.9	798.3	20.8	2.32
	27.9	816.7	25.7	2.88
	29.9	831.5	31.7	3.56
	31.9	844.2	37.1	4.20
	34.9	863.9	40.2	4.56
353	19.9	594.2	4.9	0.54
	21.9	634.9	6.7	0.74
	23.9	671.3	11.9	1.31
	25.9	699.9	13.8	1.53
	27.9	723.2	18.6	2.07
	29.9	746.5	19.4	2.16
	31.9	766.1	25.5	2.85
	34.9	788.9	32.6	3.67

Table 6. Solubility *S* (in Grams per Kilogram of Solvent) and Mole Fraction Solubility x_2 of Retinol (2) in Supercritical Carbon Dioxide (1)

T/K	*P*/MPa	ρ/kg·m^{-3}	*S*/g·kg^{-1}	$x_2/10^{-3}$
313	20.0	840.2	10.3	1.60
	22.0	857.7	12.5	1.95
	24.0	873.0	15.1	2.35
	26.0	886.7	18.5	2.88
	28.0	899.1	19.8	3.10
	30.0	910.5	21.8	3.42
	32.0	921.0	22.4	3.50
	35.0	935.4	23.8	3.73
333	20.0	723.2	10.0	1.55
	22.0	752.1	11.7	1.82
	24.0	776.0	16.0	2.50
	26.0	796.4	19.0	2.96
353	20.0	594.2	9.2	1.42
	22.0	636.8	9.4	1.46
	24.0	671.3	11.0	1.70
	26.0	699.9	13.9	2.16
	28.0	724.3	18.0	2.80
	30.0	745.5	22.3	3.49
	32.0	764.3	25.2	3.96
	35.0	788.9	27.6	4.34

There are two effects observed: At constant temperature the solubility increases with increasing density. This is probably due to the increasing solvent power of carbon dioxide at higher density. A nearly linear relationship between the density of carbon dioxide and the logarithm of the solubility was found for both tocopherols in the region of pressure and temperature investigated. At constant density (e.g. at 750 kg/m^3) a rise of temperature results in an increase in solubility. This results from the increasing vapor pressure of the solid.

Figure 2 illustrates the solubility values of α-tocopherol in carbon dioxide presented in this work at 333 K in comparison with data from literature. The data from Chrastil (1982) correspond to this work. Also the values from Zehnder (1992) at 327 K and 336 K fit to this work, especially if their deviation range is taken into consideration. The data of Pereira et al. (1993) are generally lower than this work. However, their data show variation at constant density up to 10%. Meier (1992) measured solubilities at 343 K. As expected, these values are somewhat higher than this work.

In Figure 3, the solubility of retinol (2) (vitamin A) in supercritical carbon dioxide (1) is shown as a function of the CO_2 density on a semilogarithmic scale. The solubility of retinol measured under these conditions is in the range of (9.2 to 28) g/kg, with respect to $x_2 = (1.4 \times 10^{-3}$ to $4.3 \times 10^{-3})$. The solubility increases with increasing density at constant temperature and with increasing temperature at constant density.

A similar behavior occurs for the solubility of vitamin D_3 in Figure 4. The solubilities of vitamin D_3 (2) are in the range from (4.0 to 44) g/kg, corresponding to $x_2 = (0.46 \times 10^{-3}$ to $5.2 \times 10^{-3})$.

In Figure 5, the solubility of vitamin K_1 (2) in supercritical carbon dioxide (1) at temperatures of (313, 333, and 353) K is shown as a function of pressure. The solubility of vitamin K_1 is in the range of 3.0 g/kg at 353 K and a

Table 7. Solubility *S* (in Grams per Kilogram of Solvent) and Mole Fraction Solubility x_2 of β-Carotene (2) in Supercritical Carbon Dioxide (1)

T/K	P/MPa	ρ/kg·m^{-3}	S/g·kg^{-1}	$x_2/10^{-6}$
313	20.0	840.2	0.11	0.09
	22.0	857.7	0.12	0.10
	24.0	873.0	0.13	0.11
	26.0	886.7	0.16	0.13
	28.0	899.1	0.17	0.14
	30.0	910.5	0.19	0.16
	32.0	921.0	0.29	0.24
	35.0	935.4	0.34	0.28
333	20.0	723.2	0.34	0.28
	22.0	752.1	0.43	0.35
	24.0	776.0	0.64	0.52
	26.0	796.4	0.72	0.59
	28.0	814.2	1.05	0.86
	30.0	830.0	1.26	1.03
	32.0	844.2	1.46	1.19
	35.0	863.3	1.44	1.18
353	20.0	594.2	0.42	0.35
	22.0	671.3	1.07	0.88
	24.0	699.9	1.17	0.96
	26.0	724.3	2.05	1.68
	28.0	745.5	2.45	2.01
	30.0	764.3	2.64	2.17
	32.0	788.9	3.95	3.24

Table 8. Solubility *S* (in Grams per Kilogram of Solvent) and Mole Fraction Solubility x_2 of Vitamin D_3 (2) in Supercritical Carbon Dioxide (1)

T/K	P/MPa	ρ/kg·m^{-3}	S/g·kg^{-1}	$x_2/10^{-3}$
313	20.0	840.2	5.0	0.57
	22.0	857.7	5.2	0.60
	24.0	873.0	5.0	0.57
	26.0	886.7	5.5	0.64
	28.0	899.1	6.3	0.72
	30.0	910.5	6.4	0.73
	35.0	935.4	6.9	0.79
333	20.0	723.2	4.0	0.46
	22.0	752.1	5.1	0.58
	24.0	776.0	5.8	0.67
	26.0	796.4	7.3	0.84
	28.0	814.2	9.0	1.04
	30.0	830.0	11.8	1.36
	32.0	844.2	26.4	3.09
	35.0	863.3	43.8	5.21
353	20.0	594.2	4.0	0.46
	22.0	636.8	4.1	0.47
	24.0	671.3	5.9	0.68
	26.0	699.9	6.4	0.73
	28.0	724.3	6.9	0.79
	30.0	745.5	9.3	1.08
	32.0	764.3	11.7	1.36
	35.0	788.9	25.0	2.92

Table 9. Solubility *S* (in Grams per Kilogram of Solvent) and Mole Fraction Solubility x_2 of Vitamin D_2 (2) in Supercritical Carbon Dioxide (1)

T/K	P/MPa	ρ/kg·m^{-3}	S/g·kg^{-1}	$x_2/10^{-3}$
313	20.0	840.2	3.2	0.35
	22.0	857.7	3.4	0.38
	24.0	873.0	3.8	0.42
	26.0	886.7	4.2	0.46
	28.0	899.1	4.0	0.45
	30.0	910.5	4.3	0.48
	32.0	921.0	4.6	0.51
333	20.0	723.2	2.7	0.30
	22.0	752.1	3.3	0.37
	24.0	776.0	4.3	0.48
	26.0	796.4	5.2	0.58
	28.0	814.2	5.7	0.64
	30.0	830.0	6.3	0.70
353	20.0	594.2	2.6	0.29
	22.0	636.8	4.9	0.54
	24.0	671.3	5.8	0.64
	25.0	686.2	6.9	0.77
	26.0	699.9	7.4	0.83
	28.0	745.5	9.3	1.04

Table 10. Solubility *S* (in Grams per Kilogram of Solvent) and Mole Fraction Solubility x_2 of Vitamin K_1 (2) in Supercritical Carbon Dioxide (1)

T/K	P/MPa	ρ/kg·m^{-3}	S/g·kg^{-1}	$x_2/10^{-3}$
313	20.0	840.2	13.4	1.32
	22.0	857.7	15.2	1.51
	24.0	873.0	17.0	1.69
	26.0	886.7	20.0	1.99
	28.0	899.1	22.4	2.23
	30.0	910.5	27.8	2.78
	32.0	921.0	32.3	3.25
	35.0	935.4	35.3	3.56
333	20.0	723.2	7.2	0.71
	22.0	752.1	11.2	1.11
	24.0	776.0	15.3	1.51
	26.0	796.4	17.2	1.70
	28.0	814.2	20.5	2.04
	30.0	830.0	22.6	2.25
	32.0	844.2	28.1	2.81
	35.0	863.3	34.8	3.51
353	20.0	594.2	3.0	0.29
	22.0	636.8	5.7	0.56
	24.0	671.3	9.1	0.89
	26.0	699.9	11.6	1.14
	28.0	724.3	16.4	1.62
	30.0	745.5	20.1	2.00
	32.0	764.3	24.8	2.48
	35.0	788.9	29.8	2.99

Table 11. Solubility *S* (in Grams per Kilogram of Solvent) and Mole Fraction Solubility x_2 of Vitamin K_3 (2) in Supercritical Carbon Dioxide (1)

T/K	P/MPa	ρ/kg·m^{-3}	S/g·kg^{-1}	$x_2/10^{-3}$
313	22.0	857.7	23.6	6.14
	24.0	873.0	23.9	6.21
	26.0	886.7	23.0	5.99
	28.0	899.1	25.6	6.68
	30.0	910.5	23.5	6.12
	32.0	921.0	23.3	6.07

pressure of 20 MPa up to 35 g/kg at 313 K and 333 K and a pressure of 35 MPa. The solubility of vitamin K_1 is in a range similar to those of the other compounds discussed before.

The 313 K isotherm is higher than the 333 K isotherm. The 353 K isotherm is the lowest. For all pressures in the range investigated, the solubility decreases with increasing temperature. Two effects influence the behavior: First is the decrease of the solvent power of carbon dioxide because of the decreasing density and second is the increase of solubility due to the increasing vapor pressure of vitamin K_1. In this case the decrease in the solvent power predominates over the increase in vapor pressure.

In Figure 6, the solubility of vitamin D_2 is presented as a function of pressure. The solubilities of vitamin D_2 (2) under these conditions are in the range from (2.7 to 9.3) g/kg or $x_2 = (0.3 \times 10^{-3}$ to $1.04 \times 10^{-3})$. The solubility of vitamin D_2 is marginally lower than that of vitamin D_3.

At a pressure of 20 MPa the tendency of the isotherms is similar to that seen in Figure 5. The 313 K isotherm is higher than the 333 K isotherm, and the 353 K isotherm is the lowest. The decrease of solvent power of carbon dioxide due to the decreasing density predominates over the increasing vapor pressure of vitamin D_2. But between 21 MPa and 22 MPa a crossover pressure was found. Thus, in the pressure range higher than 22 MPa the solubility at a temperature of 313 K is lower than the one at 333 K and the solubility at 353 K is the highest. Here the reversed case occurs and the increasing vapor pressure of

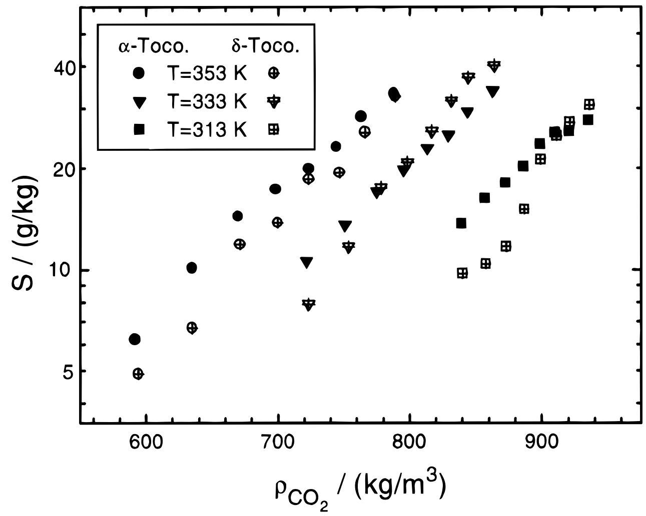

Figure 1. Solubility *S* (in grams per kilogram of solvent) of tocopherols (2) in carbon dioxide (1) as a function of density.

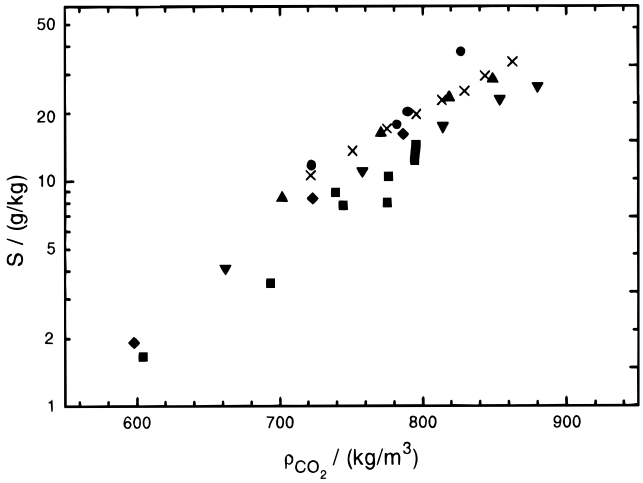

Figure 2. Solubility *S* (in grams per kilogram of solvent) of α-tocopherol (2) in carbon dioxide (1) (all data at 327 to 343 K from literature: (×) this work, 333 K; (■) Pereira et al. (1993), 333 K; (▼) Zehnder (1992), 327 K; (▲) Zehnder (1992), 336 K; (●) Meier (1992), 343 K; (♦) Chrastil (1982), 333 K).

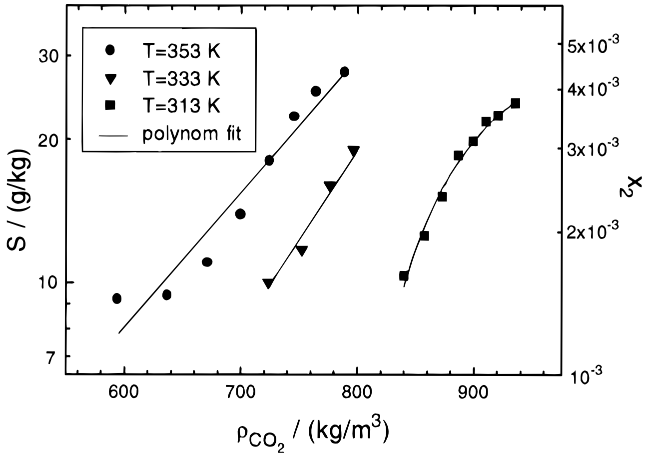

Figure 3. Solubility *S* (in grams per kilogram of solvent) of retinol (2) in carbon dioxide (1) as a function of density.

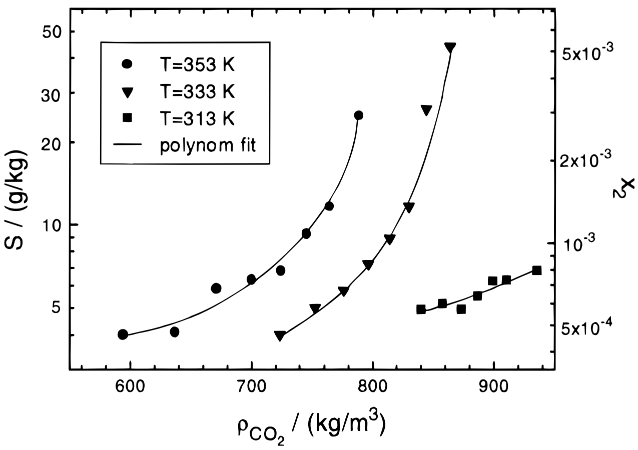

Figure 4. Solubility *S* (in grams per kilogram of solvent) of vitamin D_3 (2) in carbon dioxide (1) as a function of density.

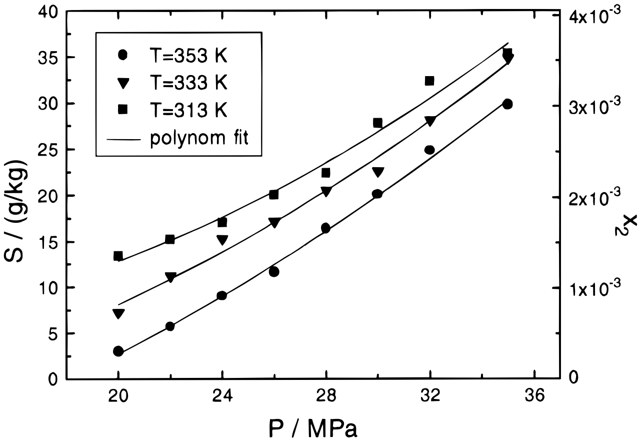

Figure 5. Solubility *S* (in grams per kilogram of solvent) of vitamin K_1 (2) in carbon dioxide (1) as a function of pressure.

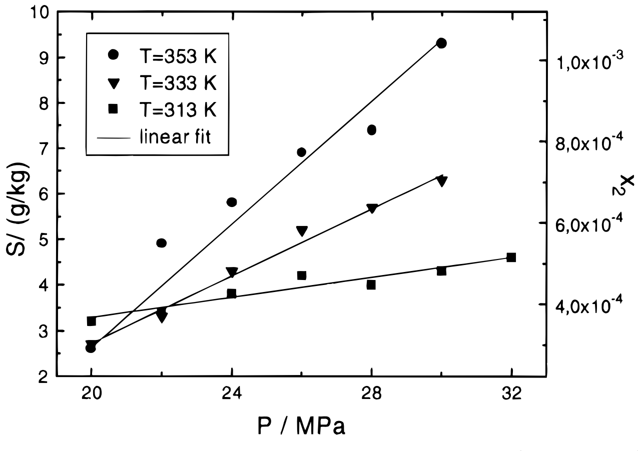

Figure 6. Solubility *S* (in grams per kilogram of solvent) of vitamin D_2 (2) in carbon dioxide (1) as a function of pressure.

vitamin D_2 predominates over the decrease of solvent power of carbon dioxide due to the decreasing density.

These two contrasting effects are also decisive if the influence of the temperature on solubility is discussed. In Figure 7, the result of experimental measurements of the solubility of δ-tocopherol in supercritical carbon dioxide is shown as a function of temperature.

At a constant pressure in the range of 313 K to 333 K the solubility increases with increasing temperature. The vapor pressure effect predominates over the density effect, as seen in the upper figure. However, in this case, a solubility maximum occurs and at temperatures greater than 333 K the solubility decreases with increasing temperature. In that case the effect of decreasing density predominates over the vapor pressure effect.

Figure 8 illustrates the solubility of β-carotene (2) in carbon dioxide (1) at different pressures as a function of

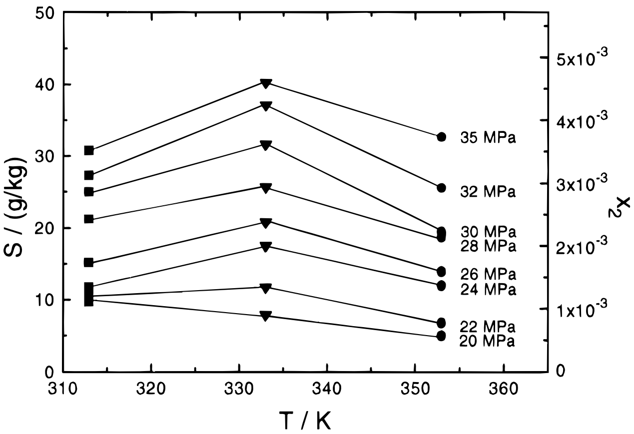

Figure 7. Solubility *S* (in grams per kilogram of solvent) of δ-tocopherol (2) in carbon dioxide (1) as a function of temperature.

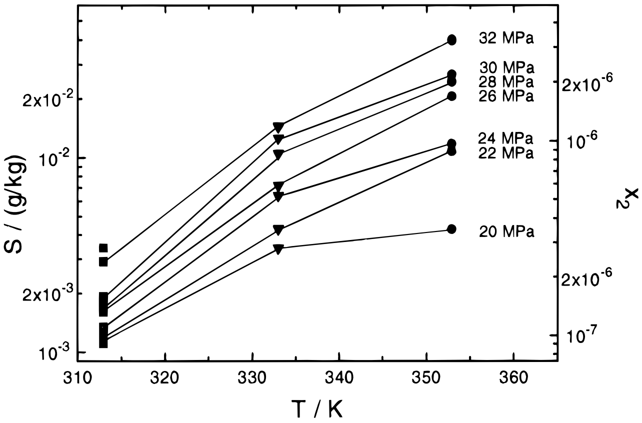

Figure 8. Solubility *S* (in grams per kilogram of solvent) of β-carotene (2) in carbon dioxide (1) as a function of temperature.

temperature. The solubility of β-carotene is in the range of (1×10^{-3} g/kg up to 4×10^{-2}) g/kg, corresponding to x_2 = (0.09×10^{-6} to 3.2×10^{-6}). The solubility is 3 orders of magnitude lower than those of the other fat-soluble vitamins.

At all pressures the solubility increases with increasing temperature although the carbon dioxide density decreases at the same time. Obviously, the increase of the vapor pressure of β-carotene exerts a greater influence on solubility than the decrease of the density of carbon dioxide here.

In Figure 9, the solubility values of β-carotene in carbon dioxide presented in this work at a temperature between 313 K and 353 K are compared with the data from literature. The values from Cygnarowicz et al. (1990) are lower than this work. Their data at a temperature of 343 K are only a little higher than ours at 333 K. The discrepancies between the data from Sakaki (1992) and this work are smaller. However, their results indicate a higher solubility. Also a higher solubility of β-carotene in carbon dioxide was found by Skerget et al. (1995). These irregular deviations could be caused by different materials or different methods used for the solubility measurements. Sampling is difficult at low-concentration samples. Our method has been proved suitable for low solubility measurements (Johannsen and Brunner, 1994a). Additionally, β-carotene is sensitive to oxygen and light.

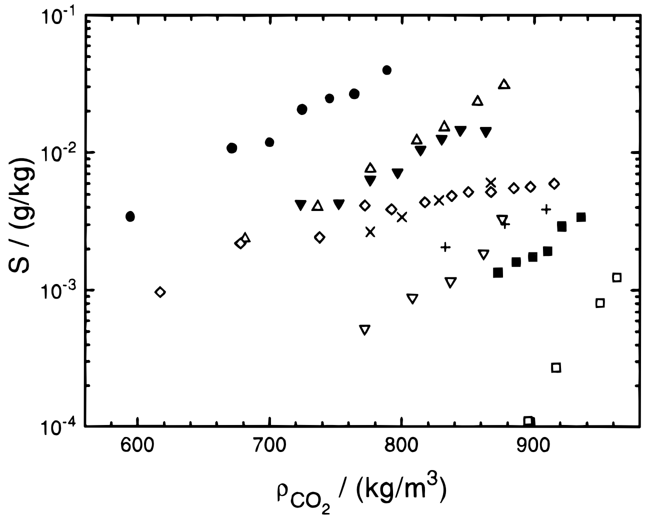

Figure 9. Solubility *S* (in grams per kilogram of solvent) of β-carotene (2) in carbon dioxide (1) (all data at 313 to 353 K from literature: this work (●) 353 K, (▼) 333 K, (■) 313 K; Cygnarowitz et al. (1990) (△) 343 K, (▽) 333 K, (□) 313 K; Sakaki (1992) (×) 323 K, (+) 313 K; Skerget et al. (1995) (◇) 313 K).

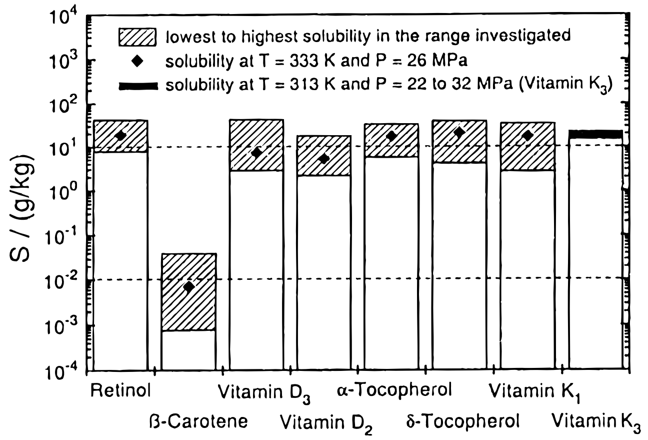

Figure 10. Solubility *S* (in grams per kilogram of solvent) of fat-soluble vitamins (2) in carbon dioxide (1).

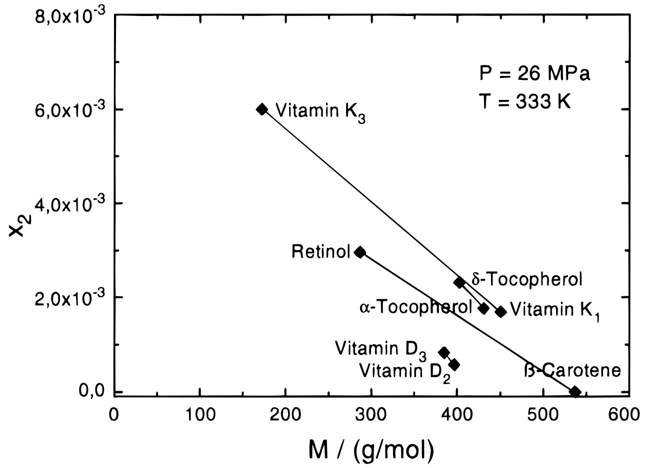

Figure 11. Mole fraction solubility x_2 of fat-soluble vitamins (2) in carbon dioxide (1) at $P = 26$ MPa and $T = 333$ K as a function of molecular mass *M*.

In Figure 10, all experimentally determined solubilities of the vitamins are shown. The solubility of vitamin K_3 has been determined only at the temperature of 313 K. The solubility behaviors of all fat-soluble vitamins except β-carotene are quite similar. Under these conditions the solubilities of these vitamins in supercritical carbon dioxide are in the range of 3 g/kg up to 40 g/kg. β-Carotene is about 3 orders of magnitude less soluble than the other vitamins. This extremely low solubility of β-carotene first of all seems to be unusual because β-carotene is a nonpolar hydrocarbon. But the high molar mass should be taken into consideration. Also, the shape of the *β*-carotene molecule could have a negative effect on the solubility.

In Figure 11, the mole fraction solubilities of the vitamins in carbon dioxide at a temperature of 333 K and a pressure of 26 MPa are shown as a function of the molecular mass. It is found that for all pairs of vitamins, the one with the higher molecular mass is less soluble. This trend is also seen in the data overall.

Conclusion

Experimental solubilities of eight different fat-soluble vitamins A, D, E, and K in supercritical carbon dioxide were measured from 313 K to 353 K and at pressures from 20 MPa to 35 MPa. The influence of temperature and density on the solubility was shown. At constant temperature, the solubility of all substances increases with increasing density. At constant density an increase in temperature results in an increase in solubility. This is a result of increasing vapor pressure of the solid.

The solubilities of all fat-soluble vitamins in supercritical carbon dioxide under the conditions investigated are in the range of 10 g/kg, except for *β*-carotene, which is 3 orders of magnitude less soluble.

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Received for review June 27, 1996. Accepted October 9, 1996.⊗ Financial support of this work by the Deutsche Forschungsgemeinschaft (Grant Br 846/9-2) is gratefully acknowledged.

JE960219M

⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1996.