

# Solubility of Capsaicin and $\beta$ -Carotene in Supercritical Carbon Dioxide and in Halocarbons<sup>†</sup>

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The solubilities of  $\beta$ -carotene and capsaicin have been measured in supercritical carbon dioxide and in difluoromethane (R-32) and 1,1,1,2-tetrafluoroethane (R-134a) in the liquid phase at temperatures near and somewhat below their critical points. The solubility of  $\beta$ -carotene was also measured in 1,1,1-trifluoroethane (R-143a). The temperatures of the measurements ranged from 35 °C to 55 °C for capsaicin (up to 85 °C in R-32) and from 40 °C to 70 °C for  $\beta$ -carotene. The solubilities were determined using an HPLC system for capsaicin and a static high-pressure cell for  $\beta$ -carotene, and the amounts of products extracted were measured spectroscopically. At similar temperatures and densities, the solubility of capsaicin in the halocarbons was higher than that in carbon dioxide; there was not such a clear trend for  $\beta$ -carotene. Where the data covered a sufficient density range, they (along with literature data for the solutes in carbon dioxide) were analyzed with the semiempirical density-based model of Méndez-Santiago and Teja.

## Introduction

The potential advantages of supercritical fluid extraction for food products and pharmaceuticals are well-known. High mass-transfer rates can be achieved due to high diffusivity and low viscosity, and the solvent density (and therefore solvent power) can be altered greatly by simply changing the pressure and/or temperature. Carbon dioxide is by far the most widely used supercritical fluid for extractions because it is nontoxic and inexpensive and has a low critical temperature. This last criterion is important for solutes that are thermally unstable at higher temperatures. One difficulty is that many polar molecules are virtually insoluble in carbon dioxide. The addition of polar entrainers, such as methanol, can increase the solubility of polar compounds. Unfortunately, these modifiers can increase the effective critical temperature, requiring higher extraction temperatures, which can damage thermally labile products. Solvent modifiers may also require downstream separation to obtain a pure product.

Halogenated hydrocarbons are another class of solvent with potential for these applications. Many are sufficiently polar to dissolve natural products and have critical temperatures that are not too high. Some are being phased out because they are believed to harm the ozone layer, but replacements with similar properties have been developed. In this work, we use three halocarbons with zero ozone-depletion potential: difluoromethane (R-32), 1,1,1,2-tetrafluoroethane (R-134a), and 1,1,1-trifluoroethane (R-143a). While all of these have critical temperatures somewhat higher than that of CO<sub>2</sub>, the experimental conditions are sufficiently near the critical temperature that substantial compressibility (and therefore variation in solubility) can be obtained.

We chose to study the solutes  $\beta$ -carotene and capsaicin because they are important natural products and are representative of products commercially extracted with liquid solvents.  $\beta$ -Carotene has no polar functional groups and represents a hydrophobic natural product. Capsaicin contains several polar groups; for this reason it is commonly extracted with alcohols and ethers.

## Experimental Section

The instrumentation used to measure solubilities has been described in detail elsewhere,<sup>1,2</sup> so only a general description will be given here. The solubility of capsaicin was measured with a modification of a commercial high-performance liquid chromatographic (HPLC) system whose reliability had been verified with the well-studied CO<sub>2</sub>/naphthalene system.<sup>1</sup> A small vessel packed with glass beads was used as a saturator and was loaded with approximately 10 mg of capsaicin. The solvent is saturated with capsaicin as it flows through the saturator; it then flows into a sampling loop where it can be injected into the HPLC system. Peak areas are measured relative to those from injections of liquid standards introduced through the normal HPLC injection port. The capsaicin was measured by ultraviolet absorption spectroscopy at 280 nm. The HPLC was operated at 25 °C with a C18 column and a mobile phase of 70% (v/v) acetonitrile and 30% water flowing at 1 mL·min<sup>-1</sup>. A Rheodyne back pressure regulator was used to maintain the HPLC system at a high enough pressure to prevent bubble formation.<sup>3</sup>

The solubility of  $\beta$ -carotene could not be measured reproducibly in the HPLC system because the relatively long residence time in the saturator led to substantial decomposition. It was instead measured by absorption spectroscopy at 450 nm in a static high-pressure cell.<sup>2</sup> This arrangement was feasible because  $\beta$ -carotene absorbs in the visible region where there is minimal absorption from the solvents or from impurities or decomposition products.

<sup>†</sup> This contribution will be part of a special print edition containing papers presented at the Fourteenth Symposium on Thermophysical Properties, Boulder, CO, June 25–30, 2000.

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**Table 1. Solubility of Capsaicin in Carbon Dioxide**

$t/^\circ\text{C}$	$p/\text{MPa}$	$s/\text{mol}\cdot\text{m}^{-3}$	$t/^\circ\text{C}$	$p/\text{MPa}$	$s/\text{mol}\cdot\text{m}^{-3}$
35	12.90	1.78	45	19.49	5.60
	13.89	2.00		21.99	7.05
	15.29	2.29		24.99	8.68
	17.00	2.61	55	12.00	1.41
	19.49	3.07		12.89	1.80
	21.99	3.46		13.89	2.19
	24.99	3.91		15.29	3.02
45	12.00	1.93		17.00	3.91
	12.89	2.29		19.49	6.31
	13.89	2.86		21.99	7.96
	15.29	3.46		24.99	9.38
	17.00	4.22			

**Table 2. Solubility of Capsaicin in R-32**

$t/^\circ\text{C}$	$p/\text{MPa}$	$s/\text{mol}\cdot\text{m}^{-3}$	$t/^\circ\text{C}$	$p/\text{MPa}$	$s/\text{mol}\cdot\text{m}^{-3}$
55	9.53	16.3	85	9.53	18.3
	10.85	17.7		10.85	22.7
	12.27	19.3		12.27	27.8
				13.38	31.0
				14.80	35.5

**Table 3. Solubility of Capsaicin in R-134a**

$t/^\circ\text{C}$	$p/\text{MPa}$	$s/\text{mol}\cdot\text{m}^{-3}$	$t/^\circ\text{C}$	$p/\text{MPa}$	$s/\text{mol}\cdot\text{m}^{-3}$
35	10.34	4.42	35	18.84	5.93
	10.34	4.46		18.72	5.81
	10.34	4.41	45	10.34	5.56
	13.89	4.82		10.34	6.80
	13.89	4.30		10.34	5.42
	13.90	5.43		13.79	7.29
	13.91	5.93		13.79	6.92
	13.92	4.12		13.79	7.09
	13.93	4.98		13.79	7.16
	13.93	5.06		17.24	7.35
	13.93	5.17		17.24	8.37
	13.93	5.35		17.24	7.74
	18.37	6.48	55	6.85	12.5
	18.41	6.60		10.41	18.0
	18.68	6.37		10.41	18.0
	18.84	6.07		13.86	38.8
	18.88	6.01		13.86	38.2

The carbon dioxide was SFC grade (>99.99% purity) from Scott Specialty Gases. Difluoromethane (R-32), 1,1,1,2-tetrafluoroethane (R-134a), and 1,1,1-trifluoroethane (R-143a) were supplied by DuPont with purities of at least 99% by mass. Capsaicin (8-methyl-*N*-vanillyl-6-noneamid, 98% purity, catalog no. M2028) and  $\beta$ -carotene (Type IV: from carrots, catalog no. C0126) were purchased from Sigma Chemical Company. All materials were used as received.

The estimated uncertainty in our temperatures is 0.5 K for the capsaicin measurements and 0.2 K for the  $\beta$ -carotene measurements. For both solutes, the uncertainty in the pressure is about 0.2 MPa. The reproducibility of the concentration measurements was approximately 5% for capsaicin in  $\text{CO}_2$ . For capsaicin in the halocarbons, it was 10–20%. For  $\beta$ -carotene, it was on the order of 30–50% in all the solvents. In general, the reproducibility was somewhat worse at higher temperatures. The analytical techniques are more precise than this; we believe these larger uncertainties are due to problems with solute reactivity and purity, as discussed in the following section.

## Results and Comparison with Other Data

Tables 1–3 show the measured solubilities of capsaicin in carbon dioxide, R-32, and R-134a. The only data found in the literature for any of these systems were solubilities in  $\text{CO}_2$  from Knez and Steiner<sup>4</sup> which, though originally given only in graphical form, were later reported in tabular

**Table 4. Solubility of  $\beta$ -Carotene in Carbon Dioxide**

$t/^\circ\text{C}$	$p/\text{MPa}$	$s/\text{mol}\cdot\text{m}^{-3}$	$t/^\circ\text{C}$	$p/\text{MPa}$	$s/\text{mol}\cdot\text{m}^{-3}$
40	6.83	$5.77 \times 10^{-6}$	70	6.18	$2.29 \times 10^{-4}$
	13.67	$1.40 \times 10^{-4}$		12.58	$2.09 \times 10^{-3}$
	20.59	$5.72 \times 10^{-4}$		19.42	$1.96 \times 10^{-2}$
	27.44	$1.05 \times 10^{-3}$		33.29	$4.26 \times 10^{-2}$
	34.29	$1.60 \times 10^{-3}$			

**Table 5. Solubility of  $\beta$ -Carotene in R-32**

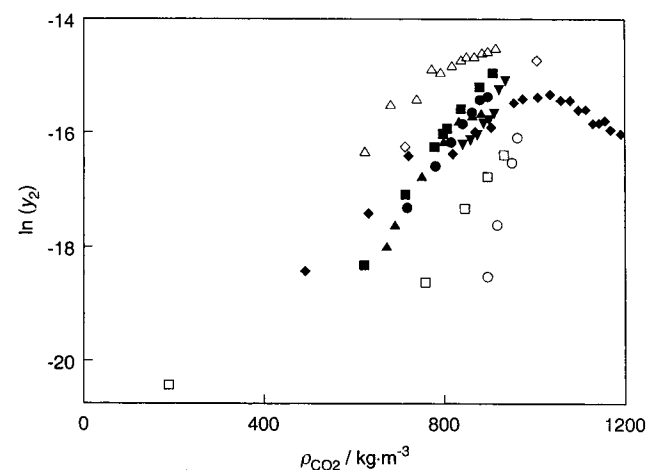
$t/^\circ\text{C}$	$p/\text{MPa}$	$s/\text{mol}\cdot\text{m}^{-3}$	$t/^\circ\text{C}$	$p/\text{MPa}$	$s/\text{mol}\cdot\text{m}^{-3}$
40	5.87	$2.72 \times 10^{-3}$	70	5.87	$4.66 \times 10^{-3}$
	9.25	$3.64 \times 10^{-3}$		12.62	$7.40 \times 10^{-3}$
	12.62	$4.12 \times 10^{-3}$		19.39	$9.00 \times 10^{-3}$
	16.00	$4.51 \times 10^{-3}$		26.20	$1.31 \times 10^{-2}$
	19.39	$4.96 \times 10^{-3}$			
	22.77	$5.22 \times 10^{-3}$			
	26.20	$5.40 \times 10^{-3}$			

**Table 6. Solubility of  $\beta$ -Carotene in R-134a**

$t/^\circ\text{C}$	$p/\text{MPa}$	$s/\text{mol}\cdot\text{m}^{-3}$	$t/^\circ\text{C}$	$p/\text{MPa}$	$s/\text{mol}\cdot\text{m}^{-3}$
40	6.40	$2.48 \times 10^{-3}$	70	6.83	$1.02 \times 10^{-2}$
	13.36	$3.53 \times 10^{-3}$		13.67	$1.23 \times 10^{-2}$
	20.35	$3.82 \times 10^{-3}$		20.59	$1.38 \times 10^{-2}$
	27.37	$4.02 \times 10^{-3}$		27.44	$1.44 \times 10^{-2}$
	34.37	$4.10 \times 10^{-3}$		34.29	$1.46 \times 10^{-2}$

**Table 7. Solubility of  $\beta$ -Carotene in R-143a**

$t/^\circ\text{C}$	$p/\text{MPa}$	$s/\text{mol}\cdot\text{m}^{-3}$	$t/^\circ\text{C}$	$p/\text{MPa}$	$s/\text{mol}\cdot\text{m}^{-3}$
40	6.18	$4.36 \times 10^{-3}$	70	6.18	$3.81 \times 10^{-3}$
	12.58	$4.82 \times 10^{-3}$		12.58	$1.03 \times 10^{-2}$
	19.42	$5.62 \times 10^{-3}$		19.42	$1.37 \times 10^{-2}$
	26.35	$5.90 \times 10^{-3}$		26.35	$1.78 \times 10^{-2}$
				33.29	$1.56 \times 10^{-2}$

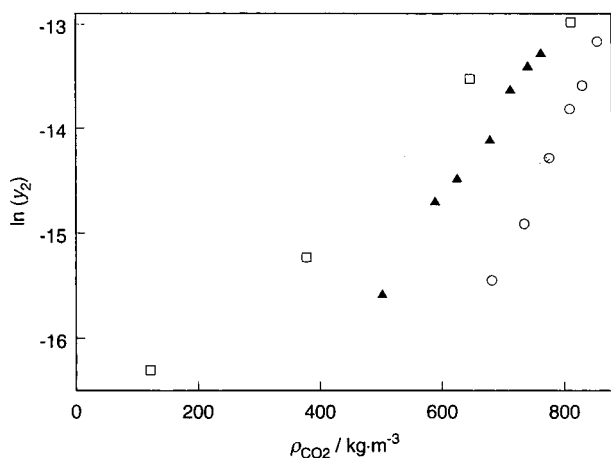


**Figure 1.** Solubility of  $\beta$ -carotene in  $\text{CO}_2$ . Measurements at 40  $^\circ\text{C}$  except where noted.  $\square$ , this work;  $\diamond$ , Cygnarowicz et al.;  $\diamond$ , Jay and Steytler<sup>7</sup> (35  $^\circ\text{C}$ );  $\nabla$ , Johannsen and Brunner;<sup>9</sup>  $\bullet$ , Mendes et al.;<sup>11</sup>  $\blacksquare$ , Sakaki;<sup>8</sup>  $\blacktriangle$ , Skerget et al.;<sup>5</sup>  $\blacktriangle$ , Subra et al.<sup>10</sup> (36.85  $^\circ\text{C}$ );  $\blacklozenge$ , Tuma<sup>12</sup> (34.45  $^\circ\text{C}$ ).

form.<sup>5</sup> These data are only roughly in agreement with our results; we defer further comparison until the next section. We observed substantial reactivity of capsaicin in the halocarbons at temperatures higher than those reported; it is possible that residual reactivity contributed to uncertainty in our reported solubilities.

Tables 4–7 show the measured solubilities of  $\beta$ -carotene in carbon dioxide, R-32, R-134a, and R-143a. Here, there are a number of experimental solubility studies in carbon dioxide<sup>5–12</sup> against which we can compare.

Figure 1 plots measured solubilities of  $\beta$ -carotene in  $\text{CO}_2$  at (and near) 40  $^\circ\text{C}$ . The density of the pure solvent at the experimental temperature and pressure,  $\rho_{\text{CO}_2}$ , is used as



**Figure 2.** Solubility of  $\beta$ -carotene in  $\text{CO}_2$ . Measurements at 70 °C except where noted.  $\square$ , this work;  $\circ$ , Cygnarowicz et al.;<sup>6</sup>  $\blacktriangle$ , Subra et al.<sup>10</sup> (66.85 °C).

the ordinate and was also used to convert the original concentration measurements to mole fraction. We computed  $\rho_{\text{CO}_2}$  from the equation of Span and Wagner.<sup>13</sup> Figure 2 is a similar plot for temperatures at and near 70 °C.

The scatter among the different data sets is striking. In Figure 1, we see that the data of Škerget et al.<sup>5</sup> lie above those of other investigators by at least a factor of 3, while the solubilities of Cygnarowicz et al.<sup>6</sup> lie well below the others (by factors from 2 to 10). The large discrepancies between these two data sets and most measurements have been noted by others. Our data show solubilities at 40 °C lower than those of most other studies (by about a factor of 2), though not as low as the data of Cygnarowicz. At 70 °C, the Cygnarowicz data again lie well below the others. At this temperature our solubilities are somewhat higher than those of Subra et al.,<sup>10</sup> though our values were lower at 40 °C.

It is difficult to pinpoint a reason for the discrepancies among data sets. The difficulty of measuring such small solubilities must be one factor. It is also difficult to obtain  $\beta$ -carotene of high purity, so impurities may have affected some or all of the data, both directly and perhaps by producing entrainer effects if the impurities are volatile. Others have speculated that the structure of the solid  $\beta$ -carotene might play a role. A crystalline solid will have a lower free energy (and therefore a lower solubility) than an amorphous solid, but crystallinity is not well preserved at higher temperatures. We found that the visual appearance of the  $\beta$ -carotene often changed upon dissolution and recrystallization, suggesting that obtaining a reproducible solid is difficult. Finally, Tuma<sup>12</sup> observed degradation and thermal rearrangement of  $\beta$ -carotene isomers in  $\text{CO}_2$ ; we also observed susceptibility to degradation from all-trans to a mixture of isomers (beginning above -40 °C) and to thermal and photochemical oxidation and decomposition. While we took pains to minimize the exposure of our samples to light, heat, and air, such effects add additional uncertainty to our data and probably those of others. All of these factors, and the scatter in the measurements from different researchers, lead us to conclude that the true solubility of  $\beta$ -carotene in supercritical  $\text{CO}_2$  is not known to within better than a factor of 2 at these conditions.

We can also compare the solubilities of the two solutes in different solvents at similar conditions. For capsaicin, the solubility at similar conditions of temperature and density is higher in the halocarbons than in  $\text{CO}_2$  by approximately a factor of 2. This makes sense physically;

the polar halocarbons should be better able to solvate the polar groups on the capsaicin molecule. For  $\beta$ -carotene,  $\text{CO}_2$  at liquidlike densities is approximately as good a solvent as the halocarbons. Since  $\beta$ -carotene is nonpolar, the polarity of the halocarbons does not significantly enhance the solubility.

We also attempted to measure the solubilities of both capsaicin and  $\beta$ -carotene in compressed hexafluoroethane (R-116), but found them to be below our detection limits. This is consistent with the behavior of perfluorocarbons in other contexts. They are known to be poor solvents for both hydrocarbons and polar solutes;  $\beta$ -carotene is essentially a large hydrocarbon, and capsaicin is a hydrocarbon with several polar groups.

## Correlation

It has long been recognized that the key variable for describing the solubility of solids in supercritical fluids is the solvent density, and plots of  $\ln(y_2)$  (where  $y_2$  is the mole fraction solubility) versus the solvent density  $\rho_1$  (or sometimes its logarithm) for individual isotherms are common.

The linearity of plots on these coordinates was first explained by Kumar and Johnston<sup>14</sup> in a derivation limited to the critical isotherm. A more general derivation was given by Harvey,<sup>15</sup> who worked with an effective Henry's constant defined by

$$k_{\text{H}}^{\text{eff}} = f_2/y_2 \quad (1)$$

where  $f_2$  is the solute fugacity, which is fixed by the presence of an equilibrium solid phase and is proportional to the vapor pressure of the pure solid. From the theory of dilute solutions near the solvent critical point, Harvey obtained

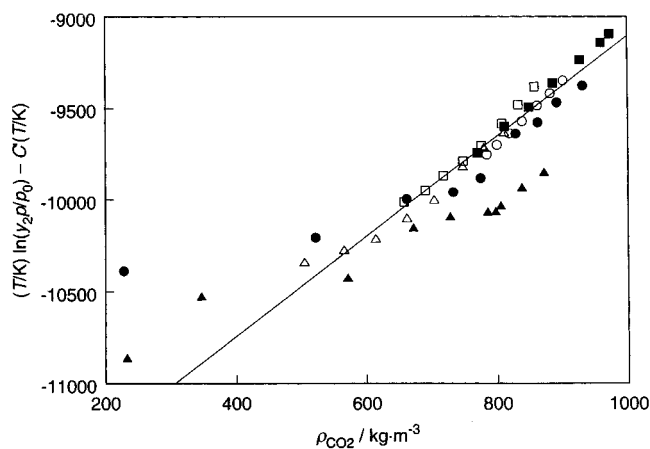
$$T \ln(k_{\text{H}}^{\text{eff}}/f_1) = A + B(\rho_1 - \rho_{\text{c},1}) \quad (2)$$

where  $\rho_{\text{c},1}$  is the solvent's critical density. Equation 2 is valid for densities near  $\rho_{\text{c},1}$ , provided the mixture critical end point is near the pure-solvent critical point (which will generally be the case if the solubility is small).<sup>16</sup> When plotted according to eq 2, data for supercritical solubility at various temperatures tended to collapse onto a single curve that was linear over a substantial range, though deviation from linearity was observed at higher densities.

A practical difficulty in applying eq 2 is that it requires the vapor pressure of the solute; this is often not known well for supercritical solubility applications. Méndez-Santiago and Teja<sup>17</sup> circumvented this problem by introducing an additional parameter for a Clausius–Clapeyron temperature dependence of the vapor pressure. They also simplified Harvey's expression by ignoring terms that varied more slowly than the leading density dependence. The final form is

$$T \ln(y_2 p/p_0) = A' + B' \rho_1 + C T \quad (3)$$

Their equation as originally written did not have the factor  $p_0$ , which we have inserted and set equal to 1 MPa in order to make the argument of the logarithm dimensionless. Equation 3 proved to be a simple, effective correlation for a wide variety of supercritical solubility data.<sup>17</sup> Its linearity with density continued fairly well up to high densities, where eq 2 lost its linearity. This was surprising, since eq 3 ignores terms from eq 2 that in principle should be included. In this work, we accept eq 3 as a simple model with some basis in theory and use it to examine and correlate our data for solubilities in  $\text{CO}_2$ . For the other



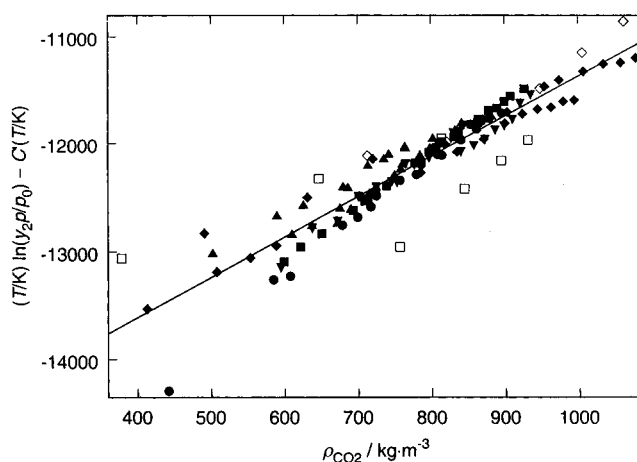
**Figure 3.** Solubility of capsaicin in supercritical CO<sub>2</sub> plotted according to eq 3. Line fitted to data from this work only. ○, this work, 35 °C; □, this work, 45 °C; △, this work, 55 °C; ■, Knez and Steiner,<sup>4</sup> 25 °C; ●, Knez and Steiner,<sup>4</sup> 40 °C; ▲, Knez and Steiner,<sup>4</sup> 60 °C.

solvents, the experiments covered only liquidlike densities varying over the range 10–20%; this range was not enough to make a density-based correlation feasible.

First, we fit our data for capsaicin solubility in CO<sub>2</sub> to eq 3. The resulting coefficients are  $A' = -11\,835$  K,  $B' = 2.7291$  K·m<sup>3</sup>·kg<sup>-1</sup>, and  $C = 25.005$ . In Figure 3, we plot our data along with those of Knez and Steiner<sup>4</sup> on the coordinates suggested by eq 3, with a straight line representing the fit. All three of our isotherms collapse nearly to the line, indicating that the model fits the data well. The solubilities of Knez and Steiner are in fair agreement at 25 °C and at 40 °C, but are lower than what our results would indicate at 60 °C. The failure of their data to collapse to a single line in Figure 3 does not necessarily mean their data lack consistency; it primarily indicates a different temperature dependence. With a smaller value of  $C$ , the Knez and Steiner data could have been fitted almost as well as our data to eq 3. We have no explanation for this moderate discrepancy between the two data sets; the purity and stability problems which make it difficult to obtain reliable data for  $\beta$ -carotene were not observed with capsaicin.

We also fit eq 3 to our solubility data for  $\beta$ -carotene in CO<sub>2</sub>, but observed that most of the data from other studies exhibited a density dependence different from that given by such a fit. Our data include two points at densities much lower than those for other measurements; without those two points the disagreement of our fit to eq 3 with other data would be less, though most other studies still exhibited higher solubility, as shown in Figure 1. The low-density data are the most uncertain, since the solubilities are very low. In addition, most of the data to which Méndez-Santiago and Teja fit eq 3 so successfully were at higher solvent densities; it is possible that the linearity does not hold at low densities.

To produce a correlation more representative of all measurements for  $\beta$ -carotene in CO<sub>2</sub>, we refit eq 3 using all the data, with a few exceptions. For the reasons mentioned above, we omit the two lowest-density points from our work. We omit all points from Škerget et al.<sup>5</sup> and Cygnarowicz et al.<sup>6</sup> since these deviate greatly from the bulk of the data. We also omit points from Tuma<sup>12</sup> at pressures above 80 MPa; his data at very high pressures are not fitted well by eq 3. This does not mean that Tuma's data are inaccurate; more likely the linearity of eq 3 is failing at these high densities.



**Figure 4.** Solubility of  $\beta$ -carotene in CO<sub>2</sub> plotted according to eq 3. □, this work; ◇, Jay and Steytler;<sup>7</sup> ▼, Johannsen and Brunner;<sup>9</sup> ●, Mendes et al.;<sup>11</sup> ■, Sakaki;<sup>8</sup> ▲, Subra et al.;<sup>10</sup> ◆, Tuma.<sup>12</sup>

Figure 4 shows the results of the new fit to eq 3, with parameters  $A' = -15\,103$  K,  $B' = 3.7309$  K·m<sup>3</sup>·kg<sup>-1</sup>, and  $C = 25.364$ . Most data fall near the fitted line. The data from our 40 °C isotherm lie noticeably below the trend, and a few individual points from other studies scatter somewhat, especially at the lowest and highest densities.

## Conclusions

We have measured the solubilities of capsaicin and  $\beta$ -carotene in supercritical carbon dioxide and in some hydrofluorocarbons. The data for capsaicin in CO<sub>2</sub> are in approximate agreement with the only previous study, though the temperature dependence appears to be different. For  $\beta$ -carotene in CO<sub>2</sub>, our solubilities at 70 °C are consistent with previous studies, while those at 40 °C are somewhat low compared to those of most previous work. There is much scatter in the literature data for  $\beta$ -carotene in CO<sub>2</sub>, probably due both to the very low solubilities and to problems with purity and stability. For both solutes in CO<sub>2</sub>, the correlation of Méndez-Santiago and Teja<sup>17</sup> proved useful for modeling the data. The polar halocarbons were better than CO<sub>2</sub> at dissolving capsaicin, while little if any difference was observed when the solute was the nonpolar  $\beta$ -carotene.

## Acknowledgment

Marcello Wood, Ryan Jacobsen, and Eric Cravens are gratefully acknowledged for their assistance with this project.

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Received for review August 4, 2000. Accepted January 3, 2001. B.N.H. was supported by a postdoctoral fellowship from the American Society for Engineering Education.

JE000255S