Densities of β-Carotene−Supercritical Carbon Dioxide Mixtures

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The densities of β-carotene−supercritical carbon dioxide mixtures were measured at (308.15, 313.15, 323.15, and 333.15) K and within the pressure range (10 to 40) MPa using a vibrating tube densimeter. The reliability of this technique has been verified in our previous work.

Introduction

Accurate data on volumetric properties are required for designing, developing, and constructing supercritical fluid processes.

β-Carotene is important for human beings because of its provitamin A activity, meaning it can be converted to vitamin A (retinol) by the body, and also because of its antioxidant activity. Vitamin A is essential for humans' normal growth and development, immune response, and vision. Supplementing lots of vitamin A is toxic, but on the other hand, the body will only convert as much β-carotene to vitamin A as it needs, which is why β-carotene is a safe source of vitamin A. Carotenoids have an important antioxidant function in plants by deactivating singlet oxygen, which is formed during photosynthesis. It is still unclear whether the biological effects of carotenoids in humans are a result of their antioxidant activity or other nonantioxidant mechanisms.[1]

The chemical structure of β-carotene is shown in Figure 1. It is a highly nonsaturated hydrocarbon containing 11 conjugated carbon−carbon double bonds. It is sensitive toward light, oxygen, and heat. β-Carotene is used as an antioxidant in conventional medical treatment for, for instance, cardiovascular diseases, cataracts, and cancer. On the other hand, there is some evidence that β-carotene, together with regular alcohol consumption and smoking, increases the risk of heart disease and cancer.

β-Carotene is an orange to red pigment, soluble in lipids and fats, and can be found in carrots, pumpkins, sweet potato, broccoli, lettuce, cabbage, spinach, tomatoes, apricots, peaches, oranges, and papayas. It is responsible for the rich colors of vegetables and fruits and is also used as a coloring agent for food.[1]

There are numerous publications concerning attractive applications connected with β-carotene, but only some of them will be mentioned here. Extensive studies have already been carried out for acquiring solubility data regarding β-carotene in carbon dioxide and also in other solvents,[2−9] binary diffusion coefficients and partition ratios,[10,11] extractions,[12−17] crystallization,[18] and synthesis and preparation of β-carotene.[19,20]

The knowledge of densities of β-carotene in supercritical carbon dioxide is important for the applications with supercritical fluids, for instance, extractions of β-carotene using supercritical carbon dioxide as a solvent. There are two different types of solutes, according to the molecular forces between the solute and supercritical solvent, the ones with attractive forces, which cause density enhancement, and the others with repulsive forces, which cause density depletion.

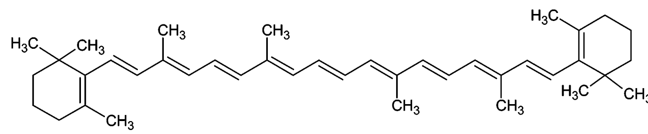

Figure 1. Chemical structure of β-carotene.

As a continuation of our work of acquiring the volumetric properties of antioxidants in supercritical fluids, we present density data regarding the mixtures of β-carotene in supercritical carbon dioxide. The densities of β-carotene in supercritical carbon dioxide were measured at (308.15, 313.15, 323.15, and 333.15) K and within the pressure range (10 to 40) MPa.

Experimental

Materials. Carbon dioxide with a purity of 99.995 % and nitrogen with a purity of 99.996 % were supplied by Messer Slovenija. β-Carotene (orange−red powder, melting point (176 to 184) °C) with stated purity ≥ 97 % and *n*-hexane with stated purity ≥ 99.5 % were obtained from Fluka. Water (purified by a Mili-Q Plus system, 18.2 MΩcm) was degassed using an ultrasonic bath. All of the chemicals were used without further purification.

Apparatus and Procedures. Densities were determined using a vibrating tube densimeter. Figure 2 shows a schematic diagram of the apparatus. The main part of the densimeter is the Anton Paar DMA 512 unit with a vibrating U-tube (5), which is connected to the electronic unit DMA 60 (6). The U-tube was thermostated using an external temperature-controlled circulating bath, which regulates temperature within $\pm\ 5 \cdot 10^{-3}$ K (7). The temperature inside the U-tube was measured with an Anton Paar CKT100 platinum resistance thermometer with an uncertainty of ± 0.01 K. Another thermostat (8) was used for thermostating the interior of the DMA 512 cell. Carbon dioxide (1) was pumped into the high-pressure cell (3) or measurement system using a high-pressure pump (2). After loading of the solid β-carotene, the high-pressure cell was evacuated by a vacuum pump, which ensures pressures to $5 \cdot 10^{-4}$ Torr (3.45 Pa), and then filled with carbon dioxide to the desired pressure. The contents of the high-pressure cell was stirred for 30 min at approximately 308 K and 20 MPa. After 30 min of rest, the upper phase was loaded in the evacuated measurement system. The pressure in the system was regulated by the use of a high-pressure Nova Swiss piston pump (4). The pressure was

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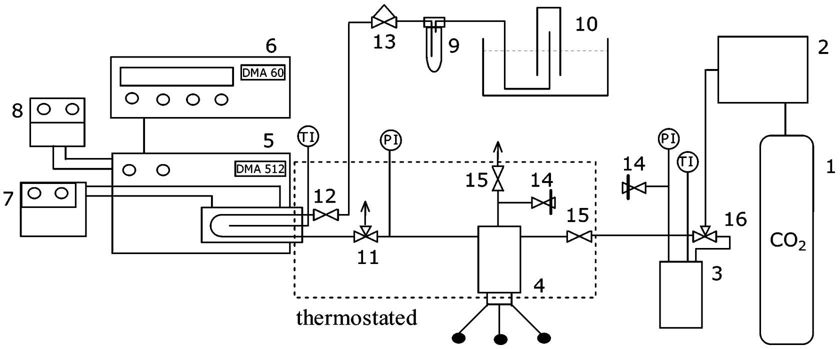

Figure 2. Schematic diagram of the apparatus: 1, CO_2 cylinder; 2, pump; 3, high-pressure cell; 4, high-pressure piston pump; 5, DMA 512 cell with U-tube; 6, electronic unit DMA 60; 7, thermostat; 8, thermostat; 9, glass trap; 10, expansion cylinder; 11, 16, three-way valve; 12, 15, valve; 13, micrometering valve; 14, safety valve.

controlled using a Wika pressure gauge. The uncertainty in the pressure measurement is estimated to be ± 0.05 MPa. At each temperature and pressure, the samples were left in the U-tube for so long that the vibration period was almost constant, so the system reached thermal equilibrium.

After the measuring procedure, the samples were expanded through valves (12, 13) to atmospheric pressure. The solute (β-carotene) was collected in a glass trap which was placed after the micrometering valve (13) and filled with solvent (*n*-hexane). The volume of expanded carbon dioxide was measured using an expansion cylinder (10). The amount of β-carotene was determined by spectrophotometric analysis. To ensure that all the solute, which could after expansion eventually stay in the U-tube, was removed, some solvent was employed. The solvent was injected through the three-way valve (11) all the way to the glass trap. Before another filling of the sample, the complete measurement system was washed out with the solvent, blown through with nitrogen, and pressurized two times with carbon dioxide to more then 20 MPa, so that the rest of the β-carotene was removed.

Finally, the density value of the pure carbon dioxide under certain conditions was checked, to be certain that the rest of the β-carotene had been removed from the measuring system.

The reference fluids used were water and nitrogen. The reported uncertainty in the density of the water is within ± 0.001 % at temperatures up to 423 K and pressures up to 10 MPa, and the uncertainties rise at higher temperatures and pressures but are generally less than 0.1 % in density, except under extreme conditions.[22] The uncertainty in the density of nitrogen is within ± 0.02 %.[23] The uncertainty in measured densities was estimated to be within ± 0.3 kg·m^{-3}.

Analytical Method. The samples collected in the glass trap were weighted on an analytical balance to within a precision of ± 1·10^{-7} kg. The amount of β-carotene in the samples was determined using a Varian Cary 1E UV−vis spectrophotometer. The absorbance was measured at 450 nm, where β-carotene has the maximum absorbance.

Results and Discussion

The densities of pure carbon dioxide and β-carotene mixtures in supercritical carbon dioxide were measured at (308.15, 313.15, 323.15, and 333.15) K and within the pressure range (10 to 40) MPa. The experimental values of the densities are listed in Table 1. The values for pure carbon dioxide at 333.15 K differ from those reported in our previous study[21] because we changed the way of thermostating the exterior of the measuring system. The maximum deviation is 0.6 % at 10 MPa, and at higher pressures the deviation becomes smaller. We cannot directly compare our values with other literature values because of different experimental conditions. The comparison is thus plotted and shown in Figure 3. Note the difference in temperature.

Table 1. Densities of β-Carotene (1) in Supercritical Carbon Dioxide (2)

T = 308.15 K		T = 313.15 K		T = 323.15 K		T = 333.15 K	
p / MPa	ρ / kg·m^{-3}	p / MPa	ρ / kg·m^{-3}	p / MPa	ρ / kg·m^{-3}	p / MPa	ρ / kg·m^{-3}
$x_1 = 0$							
10	717.2	10	636.6	10	397.3	10	296.1
15	816.1	15	781.3	15	701.8	15	607.0
20	866.1	20	840.2	20	784.9	20	724.4
30	929.0	30	909.7	30	870.3	30	829.6
40	971.7	40	955.5	40	922.8	40	889.8
$x_1 = 1.5 \cdot 10^{-6}$							
10	717.5	10	636.7	10	398.3	10	296.5
15	816.3	15	781.5	15	702.0	15	607.3
20	866.3	20	840.4	20	785.0	20	724.5
30	929.1	30	909.9	30	870.5	30	829.7
40	971.8	40	955.7	40	922.9	40	889.8
$x_1 = 2.2 \cdot 10^{-6}$							
10	717.7	10	637.3	10	397.9	10	297.2
15	816.4	15	781.6	15	701.8	15	607.7
20	866.3	20	840.4	20	784.9	20	724.7
30	929.1	30	909.9	30	870.5	30	829.7
40	971.9	40	955.7	40	923.0	40	889.8
$x_1 = 2.9 \cdot 10^{-6}$							
10	717.9	10	637.2	10	398.9	10	296.7
15	816.5	15	781.6	15	702.1	15	607.7
20	866.3	20	840.4	20	785.1	20	724.7
30	929.1	30	909.9	30	870.5	30	829.7
40	971.9	40	955.7	40	923.0	40	889.9
$x_1 = 4.3 \cdot 10^{-6}$							
10	717.6	10	637.2	10	398.2	10	296.6
15	816.4	15	781.6	15	702.0	15	607.4
20	866.4	20	840.4	20	785.0	20	724.7
30	929.1	30	909.9	30	870.5	30	829.7
40	971.9	40	955.7	40	923.0	40	889.9
$x_1 = 4.8 \cdot 10^{-6}$							
10	717.8	10	637.7	10	398.4	10	296.9
15	816.4	15	781.8	15	702.1	15	607.7
20	866.4	20	840.6	20	785.2	20	724.7
30	929.3	30	910.0	30	870.6	30	829.8
40	972.0	40	955.8	40	923.0	40	890.0
$x_1 = 5.5 \cdot 10^{-6}$							
10	718.3	10	637.8	10	398.5	10	297.0
15	816.7	15	781.9	15	702.2	15	607.8
20	866.5	20	840.7	20	785.3	20	725.0
30	929.2	30	910.1	30	870.7	30	829.9
40	972.0	40	955.9	40	923.1	40	890.0
$x_1 = 6.5 \cdot 10^{-6}$							
10	717.8	10	637.3	10	398.2	10	296.6
15	816.4	15	781.6	15	702.0	15	607.4
20	866.4	20	840.4	20	785.0	20	724.6
30	929.1	30	909.9	30	870.5	30	829.7
40	971.9	40	955.7	40	923.0	40	889.9

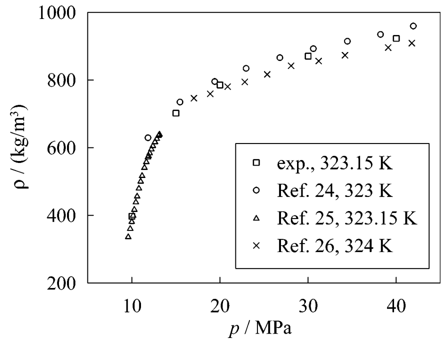

Figure 3. Comparison of experimental and literature values of the densities for pure carbon dioxide.

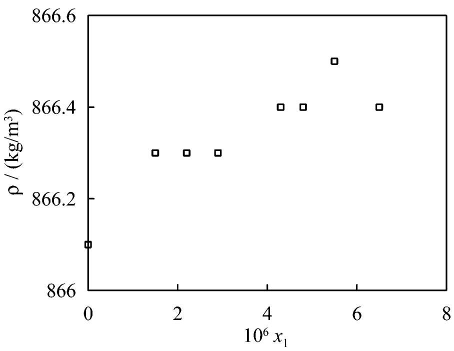

Figure 4. Densities of β-carotene in supercritical carbon dioxide at 308.15 K and 20 MPa.

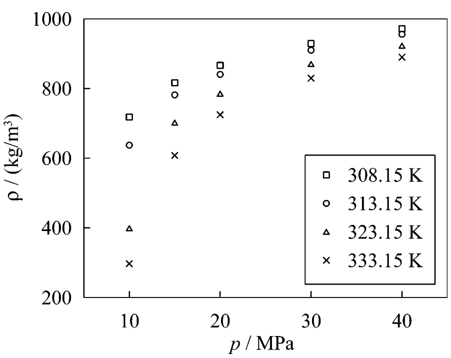

Figure 5. Densities of β-carotene (1) in a supercritical carbon dioxide (2) mixture ($x_1 = 2.9 \cdot 10^{-6}$).

As can be assessed from the data, all of the density measurements have been conducted at pressures which are higher than the critical pressure.

If we compare solubility data of β-carotene in supercritical carbon dioxide,[2-9] we can observe large discrepancies among different data sets. But mainly, the solubility lies between $1 \cdot 10^{-8}$ and $1 \cdot 10^{-5}$ of the mole fraction, considering that the solubility is higher at higher temperatures.

The concentration dependence of the densities is shown in Figure 4 at 308.15 K and 20 MPa. The values of densities rise with increasing concentration. The differences between the density of pure carbon dioxide and concentrated mixtures are small, a maximum of 1.6 $kg \cdot m^{-3}$ at lower pressures, but we must take into consideration that the mixtures are infinitely diluted.

Figure 5 shows the variation of density with pressure and temperature for β-carotene in the supercritical carbon dioxide mixture with mole fraction $x_1 = 2.9 \cdot 10^{-6}$. The density changes from (717.9 to 971.9) $kg \cdot m^{-3}$ at 308.15 K, from (637.2 to 955.7) $kg \cdot m^{-3}$ at 313.15 K, from (398.9 to 923.0) $kg \cdot m^{-3}$ at 323.15 K, and from (296.7 to 889.9) $kg \cdot m^{-3}$ at 333.15 K. The major changes in the densities regarding pressure are observed at higher temperatures.

Conclusions

The densities of pure carbon dioxide and β-carotene mixtures in supercritical carbon dioxide decrease with increasing temperature and increase with increasing pressure. The variation in density values is greater at lower pressures, in the vicinity of the critical pressure of carbon dioxide, regarding temperature, and at higher temperatures regarding pressure. Although the mixtures are infinitely diluted, we can observe density enhancement with increasing concentration of β-carotene in supercritical carbon dioxide.

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