Densities of α-Tocopherol + Supercritical Carbon Dioxide Mixtures

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The densities of α-tocopherol in supercritical carbon dioxide were measured from (308.15 to 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. The dependence of densities of α-tocopherol in supercritical carbon dioxide on composition, temperature, and pressure is presented in this study. Experimental data were correlated by the Peng–Robinson equation of state with the Panagiotopoulos−Reid mixing rule.

Introduction

α-Tocopherol is considered to be a most biologically active form of vitamin E. It is a very important fat-soluble vitamin, which encompasses a family of eight antioxidative substances: four of them are tocopherols and four are tocotrienols. These components, which are essential for the human diet, are synthesized exclusively by photosynthetic organisms.

The chemical structure of α-tocopherol is shown in Figure 1. α-Tocopherol consists of a chromanol ring (chroman ring with an alcoholic hydroxyl group) and a 12-carbon aliphatic side chain containing two methyl groups in the middle and two more methyl groups at the end of the chain. It is important for human beings because of its antioxidant activity. It helps to protect against the damaging effect of free radicals and prevents a chain reaction of lipid destruction. Vitamin E is used as an antioxidant in conventional medical treatment, for instance, cardiovascular diseases, cataracts, cancer, dementia, and diabetes, and also to enhance specific aspects of those immune responses that appear to decline as people age.

α-Tocopherol is a highly viscous brown liquid which is mainly found in vegetable oils, wheat germ, green leaf vegetables, almonds, and hazelnuts.[1]

Supercritical fluids are suitable for many different applications because of their unique physicochemical properties. With changing temperature and/or pressure, one can easily change the density, diffusivity, compressibility, viscosity, and surface tension of a supercritical fluid.

Supercritical fluids are, in comparison to conventional solvents, more acceptable in different processes because of low operating temperatures, the possibility of recovery, and the recycling of fluid and solvent-free products. For these reasons, it is possible to do sustainable or green chemistry with supercritical fluids.[2–4] The most widely used supercritical fluid is carbon dioxide because of its appropriate critical properties (low critical temperature 30.98 °C and rather low critical pressure 7.38 MPa), nontoxicity, nonflammability, and being inexpensive.

There are numerous publications about the usage of supercritical fluids, but only some of them will be mentioned here. It has been well-known for many years that supercritical fluids can be used for extracting different materials,[4–8] chemical syntheses and reactions,[9,10] the production of fine powders,[11–13]

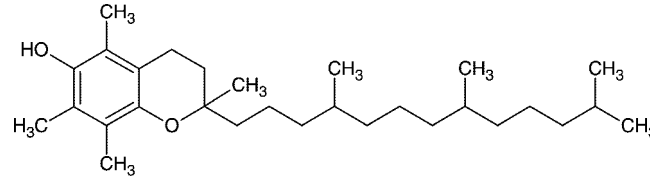

Figure 1. Chemical structure of α-tocopherol.

supercritical fluid materials processing,[10,14] and also for studying phase equilibria,[15–19] solubilities,[20–24] and acquiring fundamental properties data such as diffusion coefficients, partition coefficients, and densities.[25–31] The densities of different solutes in supercritical carbon dioxide were mainly measured by a vibrating tube densimeter like naphthalene and octacosane,[32] capsaicin,[33] styrene,[34] and 2-propanol.[35]

In this work, the densities of α-tocopherol in supercritical carbon dioxide were measured from (308.15 to 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. α-Tocopherol with a stated purity ≥ 97 % and hexane with a stated purity ≥ 99.5 % were obtained from Fluka. Methanol with a stated purity ≥ 99.9 % was obtained from Merck. Water (purified with Mili-Q Plus system, 18.2 MΩ·cm) 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. The experimental apparatus and a detailed measurement procedure were described in our previous study.[36] The main part of the densimeter was an Anton Paar DMA 512 unit with a vibrating U-tube. The temperature inside the U-tube was measured using an Anton Paar CKT100 platinum resistance thermometer with an uncertainty of ± 0.01 K. The pressure was controlled using a Wika pressure gauge. The uncertainty in the pressure measurement was estimated to be ± 0.05 MPa. At each temperature and pressure, the samples were left in the U-tube long enough for the vibration period to be almost constant, so that the system reached thermal equilibrium.

After the measuring procedure, the samples were expanded to atmospheric pressure, and the solute (α-tocopherol) was collected in a glass trap which was placed behind the microme-

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Table 1. Densities for Mixtures of α-Tocopherol (1) in Supercritical Carbon Dioxide (2)

T = 308.15 K		T = 313.15 K		T = 323.15 K		T = 333.15 K	
p	ρ	p	ρ	p	ρ	p	ρ
MPa	kg·m^{-3}	MPa	kg·m^{-3}	MPa	kg·m^{-3}	MPa	kg·m^{-3}
			$x_1 = 4.0\cdot10^{-4}$				
10	720.4	10	639.0	10	398.5	10	297.2
15	817.8	15	782.3	15	703.6	15	608.6
20	867.2	20	841.0	20	786.2	20	725.7
30	929.5	30	910.2	30	871.2	30	830.3
40	971.9	40	955.9	40	923.3	40	890.2
			$x_1 = 4.2\cdot10^{-4}$				
10	720.9	10	639.0	10	398.5	10	297.1
15	818.1	15	782.6	15	703.4	15	608.9
20	867.6	20	841.2	20	786.0	20	725.6
30	929.6	30	910.3	30	871.1	30	830.3
40	972.0	40	955.9	40	923.3	40	890.2
			$x_1 = 4.2\cdot10^{-4}$				
10	718.9	10	638.8	10	398.3	10	296.8
15	816.9	15	782.3	15	703.1	15	608.8
20	866.7	20	840.9	20	785.8	20	725.5
30	929.3	30	910.1	30	870.9	30	830.2
40	971.9	40	955.7	40	923.1	40	890.1
			$x_1 = 4.3\cdot10^{-4}$				
10	720.6	10	638.7	10	398.3	10	296.9
15	818.2	15	782.5	15	703.4	15	608.7
20	867.5	20	841.2	20	786.0	20	725.5
30	929.6	30	910.3	30	871.0	30	830.2
40	972.0	40	955.9	40	923.3	40	890.1
			$x_1 = 5.0\cdot10^{-4}$				
10	720.3	10	639.4	10	398.4	10	297.1
15	817.9	15	782.8	15	703.5	15	608.7
20	867.4	20	841.3	20	786.0	20	725.7
30	929.6	30	910.4	30	871.1	30	830.3
40	972.0	40	955.9	40	923.3	40	890.1
			$x_1 = 5.9\cdot10^{-4}$				
10	720.2	10	638.9	10	398.8	10	297.3
15	817.8	15	782.4	15	703.4	15	609.3
20	867.3	20	841.1	20	786.0	20	725.8
30	929.6	30	910.3	30	871.1	30	830.5
40	972.0	40	956.0	40	923.2	40	890.3
			$x_1 = 7.4\cdot10^{-4}$				
10	721.2	10	640.0	10	398.9	10	297.7
15	818.6	15	783.3	15	704.1	15	609.3
20	868.0	20	841.7	20	786.6	20	726.1
30	930.0	30	910.7	30	871.5	30	830.7
40	972.2	40	956.1	40	923.6	40	890.5
			$x_1 = 8.1\cdot10^{-4}$				
10	720.9	10	639.8	10	398.7	10	297.7
15	818.7	15	783.1	15	704.1	15	609.4
20	868.2	20	841.6	20	786.6	20	726.2
30	930.1	30	910.6	30	871.6	30	830.7
40	972.3	40	956.0	40	923.6	40	890.5

tering valve and filled with solvent (hexane). The amount of α-tocopherol was determined by HPLC analysis. Before introducing another sample, the complete measurement system was washed out with the solvent, blown through with nitrogen, and pressurized several times with carbon dioxide to more than 20 MPa. Finally, the density value of the pure carbon dioxide under known conditions of temperature and pressure was checked, to be certain that the rest of the α-tocopherol had been removed from the measuring system.

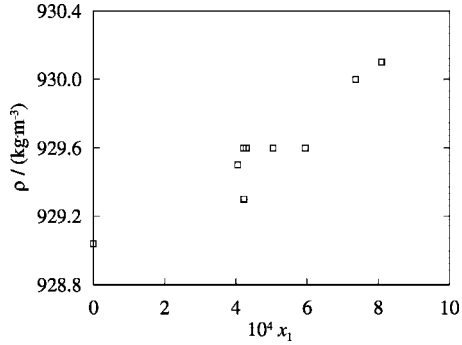

Figure 2. Densities of α-tocopherol (1) in supercritical carbon dioxide (2) at 308.15 K and 30 MPa.

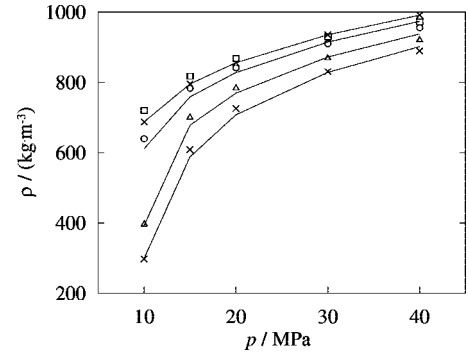

Figure 3. Densities of α-tocopherol (1) in a supercritical carbon dioxide (2) mixture ($x_1 = 5.0\cdot10^{-4}$) regarding pressure: □, 308.15 K; ○ 313.15 K; Δ, 323.15 K; ×, 333.15 K; lines calculated with the Peng–Robinson equation of state (eqs 1 to 3).

Table 2. Binary Interaction Parameters k_{12} and k_{21} (Tocopherol (1), Carbon Dioxide (2)) and AARD

T/K	k_{12}	k_{21}	AARD (%)
308.15	0.27	0.53	2.35
313.15	0.35	0.62	2.40
323.15	0.16	0.23	1.87
333.15	−0.37	0.33	1.65

Table 3. Pure Component Data Used for Correlation of the Experimental Data

component	T_c/K	P_c/MPa	ω
carbon dioxide	304.1	7.38	0.239
α-tocopherol	1257.4	0.882	0.853

The reference fluids used were water and nitrogen. The reported uncertainty in density of water is within ± 0.001 % at temperatures up to 423 K and pressures up to 10 MPa. The uncertainties rise at higher temperatures and pressures but are generally less than 0.1 % in density except under extreme conditions.[37] The uncertainty in density of nitrogen is within ± 0.02 %.[38] Uncertainty in density is estimated to be within ± 0.3 kg·m^{-3}.

Analytical Method. The samples collected in the glass trap were weighed on an analytical balance to a precision of ± $1\cdot10^{-7}$ kg. The amount of α-tocopherol in the samples was

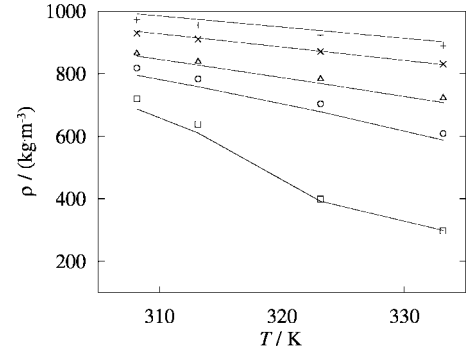

Figure 4. Densities of α-tocopherol (1) in a supercritical carbon dioxide (2) mixture ($x_1 = 5.0\cdot10^{-4}$) regarding temperature: □, 10 MPa; ○, 15 MPa; Δ, 20 MPa; ×, 30 MPa; +, 40 MPa; lines calculated with the Peng–Robinson equation of state (eqs 1 to 3).

determined using a Varian Pro Star 310 HPLC apparatus, on a UV–vis detector. The column employed was Symmetry C_{18} [(4.6·250) mm] from Waters. HPLC separation was carried out using methanol as a mobile phase at a flow rate of 1 mL·min^{-1}, at ambient temperature. The injection volume of the sample was 40 μL, and the eluent was monitored at 295 nm. Mole fraction uncertainties for the α-tocopherol + carbon dioxide mixtures were estimated to be lower than $\pm 4 \cdot 10^{-5}$.

Results and Discussion

The densities of pure carbon dioxide and mixtures of α-tocopherol in supercritical carbon dioxide were measured from (308.15 to 333.15) K and within the pressure range (10 to 40) MPa and are listed in Table 1. The experimental values of densities for pure carbon dioxide were reported in our previous study.[36] To the best of our knowledge, no density data on such mixtures have been published.

For the comparison, the mole fraction solubility of α-tocopherol in supercritical carbon dioxide lies in between $0.6 \cdot 10^{-3}$ and $3.5 \cdot 10^{-3}$.[24] The solubility is higher at higher pressures. Our density data were measured for mixtures with the mole fraction of α-tocopherol from $4.0 \cdot 10^{-4}$ to $8.1 \cdot 10^{-4}$.

The concentration dependence of the densities is shown in Figure 2 at 308.15 K and 30 MPa. The values of densities rise with increasing mole fraction of α-tocopherol. The differences in mole fraction are small, and consequently, the differences between the density of pure carbon dioxide and mixtures are small, a maximum of 3.7 kg·m^{-3}, at lower pressures and temperatures; however, we must take into consideration that the mixtures are infinitely diluted.

The dependence of densities for α-tocopherol in a supercritical carbon dioxide mixture with mole fraction $x_1 = 5.0 \cdot 10^{-4}$ regarding pressure is shown in Figure 3 and regarding temperature in Figure 4. The density changes from (720.3 to 972.0) kg·m^{-3} at 308.15 K, from (639.4 to 955.9) kg·m^{-3} at 313.15 K, from (398.4 to 923.3) kg·m^{-3} at 323.15 K, and from (297.1 to 890.1) kg·m^{-3} at 333.15 K. The major changes in the densities regarding pressure are observed at higher temperatures.

The Peng–Robinson equation of state[39] with the Panagiotopoulos−Reid mixing rule was used to correlate the experimental data.

$$p = \frac{RT}{V-b} - \frac{a}{V^2 + 2bV - b^2} \quad (1)$$

$$a = \sum_{i=1}^{2}\sum_{j=1}^{2} x_i x_j \sqrt{a_i a_j}(1 - k_{ij} + (k_{ij} - k_{ji})x_i) \quad (2)$$

$$b = \sum_{i=1}^{2}\sum_{j=1}^{2} x_i x_j \frac{b_i + b_j}{2} \quad (3)$$

Binary interaction parameters k_{12} and k_{21} were obtained by minimizing the difference between experimental and calculated data. The obtained parameters are presented in Table 2 together with the values of absolute average relative deviation

$$\mathrm{AARD} = \frac{1}{n}\sum_{i=1}^{n} \frac{|V_i^{\mathrm{exptl}} - V_i^{\mathrm{calcd}}|}{V_i^{\mathrm{exptl}}} \quad (4)$$

The Peng–Robinson equation of state requires three pure component parameters: critical temperature, critical pressure, and acentric factor. We used the values of Reid at al.[39] for carbon dioxide. For α-tocopherol, the critical temperature and pressure were calculated by the Joback method, and the acentric factor was calculated by the method of Lee and Kesler. The values are listed in Table 3.

Conclusions

The densities of α-tocopherol's 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 α-tocopherol in supercritical carbon dioxide. The experimental data have been correlated with the Peng–Robinson equation of state. The correlation showed good results although the critical properties for α-tocopherol had to be estimated with a group contribution method.

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