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Density of Water + Carbon Dioxide at Elevated Pressures: Measurements and Correlation

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Density data of the water + carbon dioxide system were determined using a calibrated vibrating tube mass flow meter with a uncertainty below 0.15%. Measurements were performed in the pressure and temperature regimes (1 to 30) MPa and (284 to 332) K, respectively. The water-rich phase density showed a pronounced dependence on pressure and temperature whereas the CO_2-rich phase density did not change from the pure density within the measuring uncertainty. A regression function was developed which describes the experimental data in the range studied.

Introduction

In the context of supercritical fluid technology developments, the two-phase system of water and carbon dioxide is of interest in various applications, such as the extraction of aqueous solutions, for example, for ethanol recovery from fermentation processes or for the purification of drinking and wastewater. There is also some relevance for dry cleaning processes and more phase catalysis. Apart from technical applications, this system plays an important role in chemical applications, especially for sea-floor CO_2 sequestration. Under the conditions relevant for the processes mentioned before, temperature and pressure below 370K and 30 MPa, respectively, the aqueous phase can be regarded as nearly incompressible, while the properties of the coexisting carbon dioxide phase are strongly dependent on density, which may easily be changed by variation of temperature and pressure. The underlying binary water + carbon dioxide system has been well-investigated in terms of mutual solubility and has been comprehensively presented in a recent review.[1] In an earlier work, we measured interfacial tension data in that system with high precision; the uncertainty was below 2%.[2] The interfacial tension depends on the density difference between the two phases. In the range of interest to us, (1 to 30) MPa and (284 to 332) K, there is slight mutual solubility of water and CO_2, but this must still not be neglected if precise experimental data are to be obtained. In this case, the density of the coexisting phases has to be known accurately. A regression function for the interfacial tension was developed, allowing for reproduction of experimental data with an accuracy better than 95%. Consequently, the objective of this study was to generate accurate density data along with an appropriate correlation.

The measuring device was adapted from a commercially available mass flow meter. The apparatus was calibrated with water within the pressure and temperature ranges of interest using more than 300 data points. Within this array the densities of both the water-rich and the carbon dioxide-rich phases were measured.

Experimental Section

Apparatus. The entire experimental device is depicted in Figure 1 and consists of a high-pressure circuit with a gear pump (A), a viewing cell (B), and a mass flow meter (C, Promass 63A, Endress+Hauser, Weil am Rhein, Germany) which uses the oscillating tube principle. The maximum pressure of the system is 30 MPa. The components and capillaries were arranged in a way that no gas bubbles could be present in the system; that is, the outlet valve (D) was the highest point of the apparatus and there were no dead volumes. The whole system was installed in a water bath. The temperature was determined using a thermocouple (Pt100, Thermocoax, Hamburg, Germany) inside the viewing cell connected to a precision thermometer (3040 and cooling block 3010, Prema, Mainz, Germany) with an accuracy of ±0.005 K. The pressure was adjusted by means of a syringe pump (E, ISCO, Axel Semrau GmbH, Sprockhövel, Germany) and measured with a calibrated, precision pressure transducer (Burster, Gernsbach, Germany) with a measuring error of ±0.05 MPa. A gear pump (A, Micropumps, Merck Eurolab, Bruchsal, Germany) was used for circulation. For the measurements, CO_2 of quality 99.9999% (Messer Griesheim, Karlsruhe, Germany) and Milli-Qplus water were used.

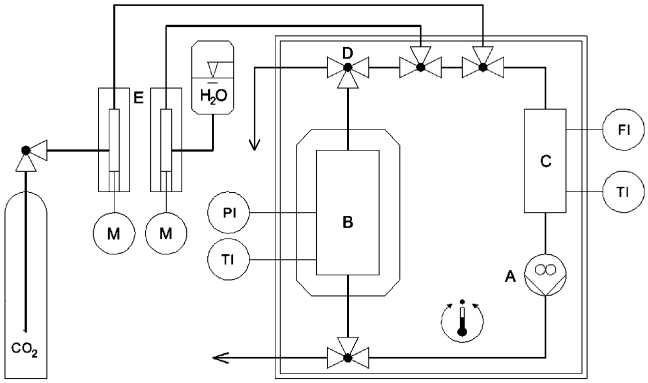

Figure 1. Measuring setup: A, gear pump; B, viewing cell; C, mass flow meter; D, outlet valve; E, syringe pump.

Experimental Procedure. Both phases, the mutually saturated water and CO_2 phases, were measured separately. The water-rich phase was measured as follows: the temperature was set and the system was filled completely with water. The pressure of the system was adjusted with the syringe pump by adding CO_2 up to the desired pressure. The mixture within the apparatus was homogenized by

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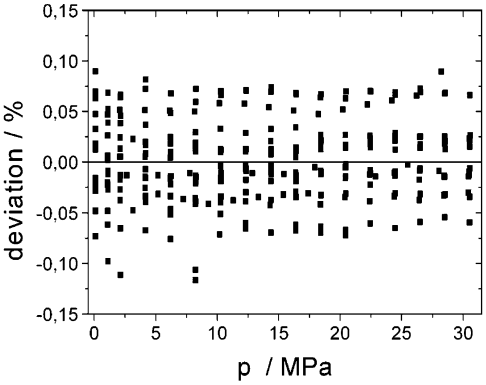

Figure 2. Calibration error of the mass flow meter for the temperature range 278 to 333 K.

recirculating the water phase with the gear pump. After waiting for a maximum of 2 h, equilibrium conditions were established; that is, no change in density and pressure occurred. Then the density value was recorded. At a constant temperature the pressure range from (1 to 30) MPa was measured in steps of 1 MPa. Thereafter the pressure was released using the same steps in order to test for a hysteresis. Both values agree within the measuring accuracy. At temperatures below 283 K and pressures higher than 4 MPa solid gas-hydrates (clathrates) are formed. These led to pluggings of the tubing, and no measurements could be performed thereafter. Measurements were taken up to the point of clathrate formation. In addition, individual measurements were performed in the vicinity of the CO_2 vapor−liquid coexistence line to clarify its influence in detail.

The CO_2-rich phase was measured in a similar way. The viewing cell was filled with water well below the mass flow meter to saturate the CO_2 with water. By pumping this phase through the mass flow meter, the density of water-saturated CO_2 was measured.

Calibration and Reproducibility of the Measurements. To obtain a high accuracy for the measurements, the density sensor was calibrated for the entire temperature range with pure water.[3] Eventually, 300 measuring points were taken into account for the calibration. The relative error of a measurement after calibration is less than 0.15% for pure water (see Figure 2).

To check for reproducibility, the isotherm at 293 K has been measured three times. The reproducibility was found to be better than ±99.93%. Therefore, the measuring error of ±0.15% appears to be reasonable for all measurements.

Results

Within the experimental uncertainty no change in the density between water-saturated CO_2 and pure CO_2 as taken from Span et al.[4] could be measured. This is in accordance with the data of King et al.[5] and can be expected because of the low mass solubility of water in compressed CO_2.[6]

For the water-rich phase 10 isotherms at 284 K, 285 K, 288 K, 293 K, 294 K, 303 K, 313 K, 323 K, 332 K, and 333 K were measured in the pressure range (1 to 30) MPa. Most of the measured data are compiled in Table 1. For all isotherms the density of CO_2-saturated water is higher than that of pure water.

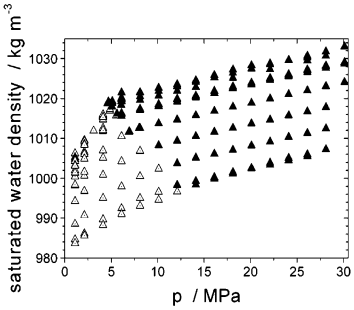

Figure 3. CO_2-saturated water density as a function of pressure. Data are taken from Table 1. Data used for eq 3 (▲) and eq 4 (△). The temperature ranges from 284 K to 333 K.

The density of the water phase depends strongly on the coexisting CO_2 phase. The increase in water density with pressure is steep in contact with a gas such as CO_2 and moderate for liquefied CO_2. The curves in Figure 3 exhibit a sharp bend at the phase transition point of CO_2 and are continuous for isotherms at temperatures higher than 304 K. The difference in the slopes is more pronounced at lower temperatures. If the density of the coexisting CO_2 is high, the slope is nearly linear and nearly the same for all isotherms. The deviation between the pure and the CO_2-saturated water densities is large at low temperatures and high pressures, with a maximum of 1.9% at 284 K and 30 MPa.

Discussion

Comparison with Published Data. Table 2 reports all papers related to the densities of the water-rich phase in CO_2 + water systems under similar conditions of temperature and pressure along with the experimental range, the method applied, and the uncertainty of the measurements. The data of Tegetmeier[6] had to be extracted from figures. All reported densities are higher than those of pure water. Thus, the uptake of CO_2 into the water phase causes an increase in the liquid-phase density—as expected.

Yaginuma et al.[6] used a vibrating tube density meter and a variable-volume viewing cell. There was no sampling, and the pressure was increased by a decrease in volume. The density was obtained during pumping the liquid phase through the density meter. They measured only the isotherm at the critical temperature of CO_2 up to 10 MPa. The data are reliable, as they published pure water density data as well, with a mean deviation of ±0.03% from the steam tables. The data in this paper and Yaginuma's match within the uncertainty.

Tegetmeier et al.[8] employed a magnetic suspension balance and Archimedes' law. The mixed density was determined via the buoyancy forces of a sinker. Their experimental error is given as ±2.5%. These data deviate most from all the other data.

Teng et al.[7] only measured the water in contact with liquid CO_2. Their apparatus consists of a sapphire tube with a water column and a CO_2 column. The pressure was adjusted with a mercury column, which is in contact with the water phase. The increase in density of the water-rich phase was observed by the volume change indicated by the shift in the position of the interface. The given uncertainty is ±1.9%. Their data display a smaller slope in the CO_2-saturated water density. The influence of hydrate formation on the measurement is probably not negligible, as the authors suggested.

King et al.[5] utilized recirculation equipment and an off-line sampling method for the determination of the density. Care was taken that the sampling procedure should not interfere with the equilibrium conditions. The density was measured by using a density bottle technique. Their uncertainty is given as ±0.5%.

Regression Function for CO_2-Saturated Water. Data of all authors with uncertainties below ±1% were taken into account for the regression, comprising in total 206 data points. To consider the different measuring uncertainties,

Table 1. Measured Isotherms

T/K	p/MPa	ρ_{H_2O}/kg·m^{-3}	T/K	p/MPa	ρ_{H_2O}/kg·m^{-3}	T/K	p/MPa	ρ_{H_2O}/kg·m^{-3}	T/K	p/MPa	ρ_{H_2O}/kg·m^{-3}
284.35	5.21	1019.32	292.89	12.36	1019.73	312.74	10.33	1008.19	vapor−liquid coexistence line		
284.05	6.23	1020.20	292.89	14.41	1020.70	312.74	12.38	1009.36	283.01	1.13	1005.23
284.04	8.25	1021.57	292.99	14.42	1020.60	312.77	14.41	1010.54	283.02	2.14	1008.52
283.97	10.26	1022.65	292.85	16.44	1021.87	312.74	16.43	1011.61	283.03	6.22	1020.06
284.04	12.30	1023.52	292.93	16.46	1021.87	312.75	18.46	1012.59	283.02	8.26	1021.53
284.04	14.24	1024.52	292.84	18.48	1022.64	312.85	20.40	1013.69	284.38	4.18	1015.54
283.99	16.37	1025.86	292.91	18.42	1022.96	312.54	22.46	1014.64	284.50	4.76	1019.07
284.05	18.40	1027.24	292.88	20.47	1023.93	312.74	24.46	1015.73	284.47	4.83	1019.14
283.87	20.42	1028.31	292.91	20.47	1023.93	312.88	26.49	1016.71	284.67	5.23	1019.23
283.95	22.46	1028.78	292.84	22.49	1025.10	312.83	28.48	1017.80	284.70	6.23	1019.82
283.91	24.47	1029.66	292.93	22.47	1024.91	322.80	1.10	988.52	284.48	1.10	1004.79
283.80	26.49	1030.33	292.85	24.49	1026.09	322.81	2.10	990.71	284.47	2.11	1008.28
284.86	1.10	1004.81	292.98	24.49	1025.89	322.90	4.18	995.07	284.59	4.10	1015.77
284.86	2.12	1009.49	292.90	26.51	1027.06	322.85	6.22	997.94	284.58	4.10	1015.97
284.91	4.14	1014.67	292.92	26.53	1027.26	322.79	8.26	1000.51	284.48	4.71	1018.78
284.93	6.18	1019.24	292.88	28.55	1028.23	322.84	10.28	1002.38	284.58	5.16	1018.85
284.94	8.22	1020.51	292.90	28.53	1028.14	322.85	12.33	1003.75	284.54	6.22	1019.42
284.94	10.29	1021.88	292.86	30.58	1029.11	322.85	14.40	1005.11	284.91	1.07	1004.32
284.91	12.37	1023.03	293.93	1.11	1000.44	322.78	16.41	1006.09	284.63	2.09	1009.19
284.91	14.48	1024.18	293.92	2.12	1006.03	322.81	18.43	1007.07	284.51	3.11	1011.88
284.90	16.52	1025.25	293.88	4.16	1011.80	322.84	20.44	1008.15	284.38	4.72	1019.07
284.91	18.54	1026.43	293.84	6.18	1015.57	322.84	22.45	1009.13	284.42	6.23	1019.81
284.89	20.55	1027.51	293.84	8.24	1017.04	322.94	24.50	1010.30	287.73	1.08	1003.32
284.89	22.57	1028.58	293.85	10.28	1018.01	322.94	26.53	1011.27	287.63	2.11	1008.50
284.92	24.59	1029.66	293.84	12.32	1019.18	322.84	28.55	1012.45	287.81	4.18	1015.37
283.89	26.61	1030.70	293.82	14.34	1020.25	331.85	1.18	984.63	287.71	4.91	1016.84
283.90	28.64	1031.77	293.82	16.38	1021.33	331.85	2.19	986.11	287.75	5.21	1017.95
283.93	30.66	1033.05	293.82	18.40	1022.50	331.85	4.20	989.69	292.85	1.11	1001.40
287.76	1.09	1003.12	293.82	20.44	1023.47	331.83	6.26	992.46	292.94	2.16	1004.88
287.75	2.13	1008.30	293.85	22.44	1024.56	331.83	8.31	995.03	292.85	4.18	1011.95
287.68	4.18	1015.26	293.84	24.45	1025.54	331.82	10.32	996.60	292.87	5.66	1015.70
287.69	4.90	1017.24	293.83	26.48	1026.61	332.15	12.31	998.30	292.75	5.76	1016.16
287.66	5.20	1017.95	293.83	28.52	1027.68	332.15	14.34	999.28	292.76	8.36	1017.36
287.84	6.16	1018.36	293.84	30.53	1028.76	332.15	16.36	1000.25	303.17	1.11	998.38
287.79	8.23	1019.62	302.85	1.12	998.17	332.16	18.39	1001.53	303.06	2.15	1001.66
287.68	10.27	1020.68	302.78	2.15	1000.65	331.75	20.41	1002.59	302.61	4.20	1006.91
287.65	12.31	1021.85	302.68	4.18	1005.12	331.66	22.42	1003.86	302.75	6.28	1010.47
287.73	14.27	1022.85	302.73	6.25	1010.48	332.06	24.46	1005.05	302.76	7.10	1011.52
287.72	18.33	1025.20	302.75	8.26	1012.56	332.15	26.47	1005.93	302.61	7.17	1011.69
287.69	22.35	1027.36	302.79	10.32	1013.73	332.15	28.47	1007.22	302.76	8.26	1012.56
287.68	26.39	1029.51	302.79	12.36	1014.70	333.23	1.11	983.70			
287.76	28.39	1030.69	302.75	14.38	1015.77	333.19	2.15	985.58			
292.85	1.17	1001.98	302.77	16.44	1016.84	333.10	4.19	988.24			
292.91	1.11	1000.50	302.79	18.46	1017.92	333.02	6.24	991.01			
292.83	2.14	1005.98	302.87	20.49	1018.89	333.13	8.27	993.09			
292.86	2.19	1006.57	302.84	22.52	1019.96	333.04	10.31	994.55			
292.87	4.19	1012.55	302.81	24.52	1021.05	333.09	12.35	996.63			
292.94	4.22	1012.55	302.82	26.54	1022.02	333.12	14.39	998.40			
292.81	6.29	1016.30	302.77	28.55	1023.10	333.03	16.41	999.87			
292.89	6.26	1016.11	302.79	30.50	1024.10	333.03	18.44	1001.14			
292.83	8.34	1017.37	312.89	1.10	994.25	333.03	20.46	1002.52			
292.87	8.28	1017.39	312.77	2.17	996.81	333.02	22.47	1003.40			
292.81	10.39	1018.54	312.75	4.19	1000.89	333.02	24.49	1004.48			
292.87	10.31	1018.46	312.74	6.25	1004.25	333.02	26.51	1005.45			
292.69	12.42	1019.91	312.73	8.30	1006.82						

these were assigned as weights. The least-squares fit method was used without restraints to obtain the fit parameters. The Marquart method was employed for the regression. The relative error in CO_2-saturated water associated with the regression function (eqs 3 and 4) is defined as

$$r_0 \equiv \frac{x_{\mathrm{reg}} - x_{\mathrm{exp}}}{x_{\mathrm{exp}}} \qquad (1)$$

where x_{reg} and x_{exp} are the predicted and experimental values for a specific datum, respectively. The weighted standard deviation of the relative density error, σ, is calculated from

$$\sigma = \left(\frac{\sum_i w_i^2 r_{0,i}^2}{\sum_i w_i^2}\right)^{0.5} \qquad (2)$$

where w_i is the published measuring uncertainty of datum i. Solution of eq 2 shows that the regression fits all the

Table 2. Published Data of the CO_2-Saturated Water Density

author, reference	pressure range, MPa	temperature range/ K	data	method	uncertainty/%
King et al.[5]	6 to 24	288.1, 293.1, 298.1	27	off-line gravimetric and volumetric	±0.5
Yaginuma et al.[6]	1.0 to 10.0	304.1	14	vibrating tube density meter with a variable-volume cell	±0.1
Teng et al.[7]	6.4 to 29.5	278, 283, 288, 293	24	increase of water phase volume due to CO_2 uptake	±1.87
Tegetmeier et al.[8]	0 to 30	294, 313, 332, 354, 374	38	magnetic suspension balance using Archimedes' law	±2.5
this work	1 to 30	284, 285, 288, 293, 294, 303, 313, 323, 332, 333	165	vibrating tube density meter with addition of CO_2 for pressure adjustment	±0.15

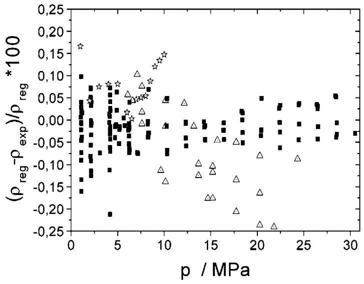

Figure 4. Relative deviation of the regression function (eqs 3 and 4): ■, this work; △, King; ☆, Yaginuma. The measuring conditions are listed in Table 2.

Table 3. Coefficients of the Regression Function (Eqs 3 and 4)

coefficient	value
l_0/kg·m^{-3}	949.7109
l_1/kg·m^{-3}·MPa^{-1}	0.559 684
l_2/kg·m^{-3}·K^{-1}	0.883 148
l_3/kg·m^{-3}·MPa^{-2}	−0.000 97
l_4/kg·m^{-3}·K^{-2}	−0.002 28
g_0/kg·m^{-3}	805.1653
g_1/kg·m^{-3}·MPa^{-1}	44.126 85
g_2/kg·m^{-3}·K^{-1}	1.573 145
g_3/kg·m^{-3}·MPa^{-2}	−1.450 73
g_4/kg·m^{-3}·K^{-2}	−0.003 13
g_5/kg·m^{-3}·MPa^{-1}·K^{-1}	−0.196 58
g_6/kg·m^{-3}·MPa^{-3}	6.27×10^{-5}
g_7/kg·m^{-3}·MPa^{-1}·K^{-2}	0.000 209
g_8/kg·m^{-3}·MPa^{-2}·K^{-1}	0.004 204

experimental data with a standard deviation of ±0.2% (Figure 4).

It was not possible to describe the data with one common algebraic function to obtain the desired high quality of reproduction. Therefore, we divided the data set into two regions: data comprising CO_2 with densities below the critical density (eq 4) and above the critical density (eq 3). The two functions are separately defined within their domains. They are neither continuous nor differentiable. The coefficients of the regression function are compiled in Table 3.

Equation 3 covers the data where the CO_2 phase is either liquid or compressed vapor and exhibits densities of higher than 468 kg·m^{-3}, the critical density of pure CO_2

$$\rho_{H_2O} = l_0 + l_1 p + l_2 T + l_3 p^2 + l_4 T^2 \tag{3}$$

Equation 4 is valid for densities lower than the critical density with respect to the CO_2-phase

$$\rho_{H_2O} = g_0 + g_1 p + g_2 T + g_3 p^2 + g_4 T^2 + g_5 pT + g_6 p^3 + g_7 T^2 p + g_8 T p^2 \tag{4}$$

In these regression functions, ρ_{H_2O} is the CO_2-saturated water density, T is the temperature in K, and p the pressure in MPa. $l_{0...4}$ and $g_{0...8}$ are coefficients; their units are given in Table 3.

The correlation yields values with a quality of reproduction above 99.75%.

Conclusion

Measurements of the density of both the water-rich and CO_2-rich phases in the two-phase region of the system CO_2 + H_2O are reported. In accordance with earlier publications by King et al.,[4] there is no measurable change of the density of the CO_2-rich phase within the experimental range. This is due to the low and almost unchanging solubility of water in CO_2. For the water-rich phase there is an increase in density with pressure under all experimental conditions. This increase can be split into two areas: whether CO_2 is gaseous or liquefied. More than 220 data points from our own measurements as well as from published data were used to generate a regression function for the temperature and pressure dependence of the water phase density. This regression function allows interpolated data to be picked precisely and therefore improves the description of the water + carbon dioxide system and in particular the accurate calculation of the interfacial tension. In a next step both the regression function of density and that for interfacial tension will be combined to allow for a precise description of the interfacial tension data.

Literature Cited

(1) Diamond, L. W.; Akinfiev, N. N. Solubility of CO_2 in water from −1.5 to 100 °C and from 0.1 to 100 MPa: evaluation of literature data and thermodynamic modeling. *Fluid Phase Equilib.* **2003**, *208*, 265−290.
(2) Hebach, A.; Oberhof, A.; Dahmen, N.; Kögel, A.; Ederer, H.; Dinjus, E. Interfacial Tension at Elevated Pressures-Measurements and Correlations in the Water + Carbon Dioxide System. *J. Chem. Eng. Data* **2002**, *47*, 1540−1546.
(3) *ASME Steam Table*, 6th ed.; The American Society of Mechanical Engineers: New York, 1992.
(4) Span, R.; Wagner, W. A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1509−1596.
(5) King, M. B.; Mubarak, A.; Kim, J. D.; Bott, T. R. The Mutual Solubilities of Water with Supercritical and Liquid Carbon Dioxide. *J. Supercrit. Fluids* **1992**, *5*, 296−302.
(6) Yaginuma, R.; Sato, Y.; Kodama, D.; Tanaka, H.; Kato, M. Saturated Densities of Carbon Dioxide + Water Mixture at 304.1 K and Pressures to 10 MPa. *Nippon Enerugi Gakkaishi* **2000**, *79* (2), 144−146.
(7) Teng, H.; Yamasaki, A.; Chun, M.-K.; Lee, H. Solubility of liquid CO_2 in water at temperatures from 278 K to 293 K and pressures from 6.44 MPa to 29.49 MPa and densities of the corresponding aqueous solutions. *J. Chem. Thermodyn.* **1997**, *29*, 1301−1310.
(8) Tegetmeier, A.; Dittmar, D.; Fredenhagen, A.; Eggers, R. Density and volume of water and triglyceride mixtures in contact with carbon dioxide. *Chem. Eng. Process.* **2000**, *39*, 399−405.
(9) Bamberger, A.; Sieder, G.; Maurer, G. High-pressure (vapor liquid) equilibrium in binary mixtures of (carbon dioxide water or acetic acid) at temperatures from 313 to 353 K. *J. Supercrit. Fluids* **2000**, *17*, 97−110.

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