Supplementary material to: Diffusion of the carbon dioxide - carbon mixture in the extended critical region

René Spencer Chatwell[1], Gabriela Guevara-Carrion[1], Yuri Gaponenko[2], Valentina Shevtsova[2] and Jadran Vrabec[1]

[1] *Thermodynamics and Process Engineering, Technische Universität Berlin, 10587 Berlin, Germany*

[2] *Microgravity Research Center, Université de Bruxelles, 1050 Bruxelles, Belgium*

CONTENTS

This supplementary material includes a schematic of the employed Taylor dispersion apparatus described in the manuscript. The enthalpy h, specific volume v as well as the response functions c_p, c_v, α_v and β_T along the studied isobar are also graphically shown. The center-of-mass radial distribution function and average coordination number of the CO_2-ethanol pair are depicted to complement the remaining molecular pairs of the mixture. Further, predictions of the Fick diffusion coefficient of the CO_2 + ethanol mixture with the regarded equations are shown in comparison with experimental and simulation results. The numerical data from molecular simulation are also listed here.

EXPERIMENTAL SET-UP

The Taylor dispersion apparatus that was used in this work is depicted in Figure S1. It consisted of four modules: a carrier fluid conditioning device, the CO_2 delivery system with a solute injection valve, the air bath thermostat housing the diffusion capillary and a FT-IR detector.

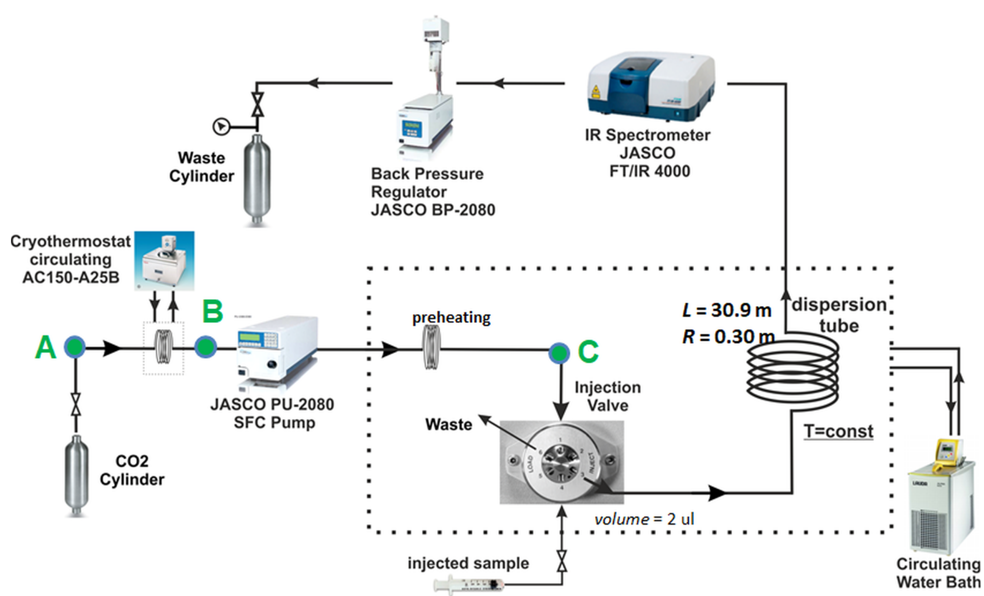

FIG. S1. Schematic of the high pressure Taylor dispersion apparatus.

RESPONSE FUNCTIONS

Thermodynamic response functions were obtained from equilibrium molecular dynamics simulations in the NpT and NVT ensembles performed with the simulation program $ms2$. Extensive equilibrium molecular dynamics simulations were performed in both ensembles during this work. In the NVT ensemble, the isochoric heat capacity c_v was determined from fluctuations of the residual potential energy and the virial. In the NpT ensemble, the residual isobaric heat capacity c_p, the isothermal compressibility β_T and the volume expansivity α_v are functions of other ensemble fluctuations. For a detailed information the interested reader is encouraged to read our publications on the features of the $ms2$ software [1].

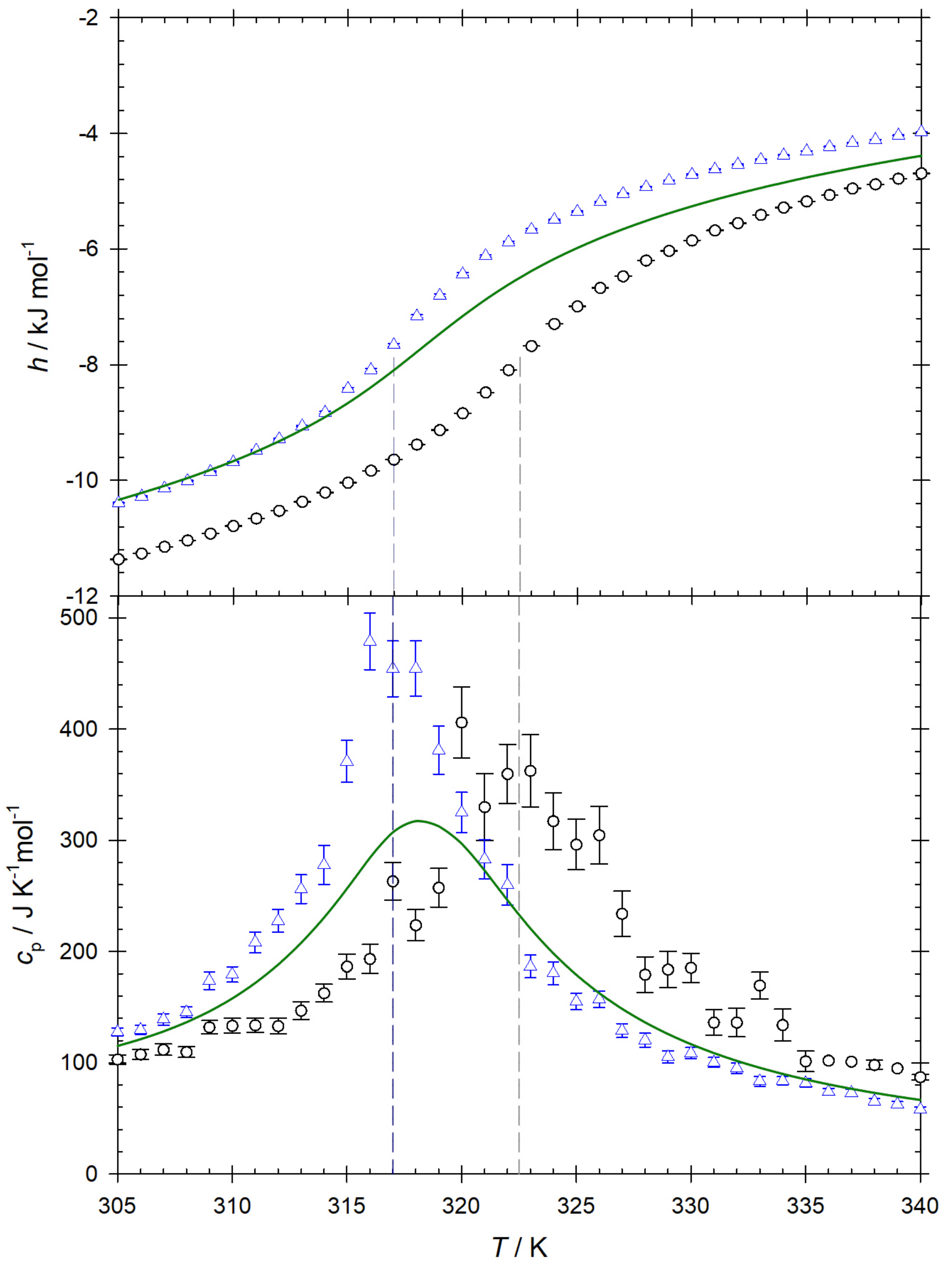

FIG. S2. Enthalpy h and isobaric heat capacity c_p of CO_2 (blue) and the mixture CO_2 + ethanol (black) along the isobar $p = 10$ MPa. The green line represents the properties of pure CO_2 calculated with the Span-Wagner equation of state [2].

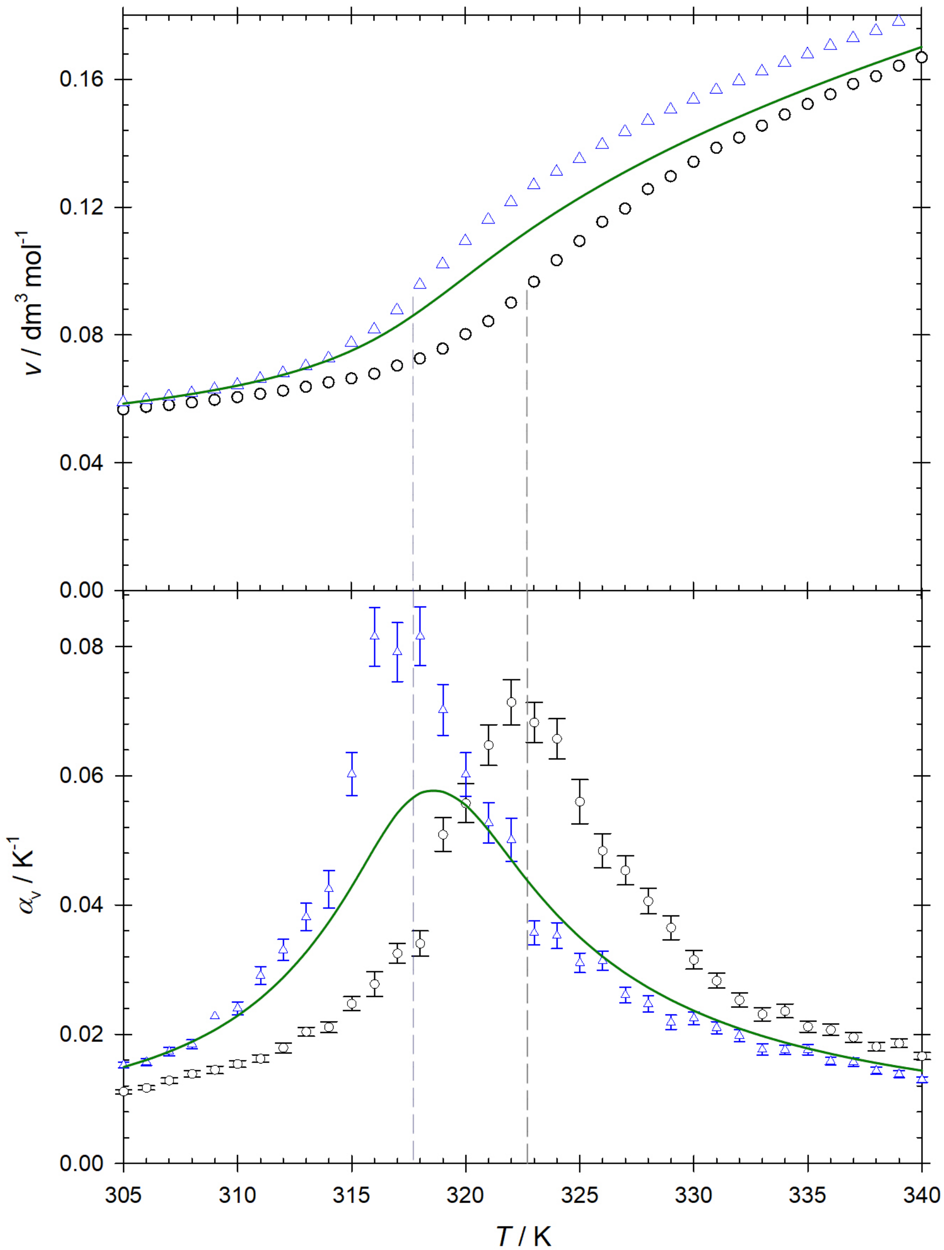

FIG. S3. Specific volume v and thermal expansion α_v of CO_2 (blue) and the mixture CO_2 + ethanol (black) along the isobar $p = 10$ MPa. The green line represents the properties of pure CO_2 calculated with the Span-Wagner equation of state [2].

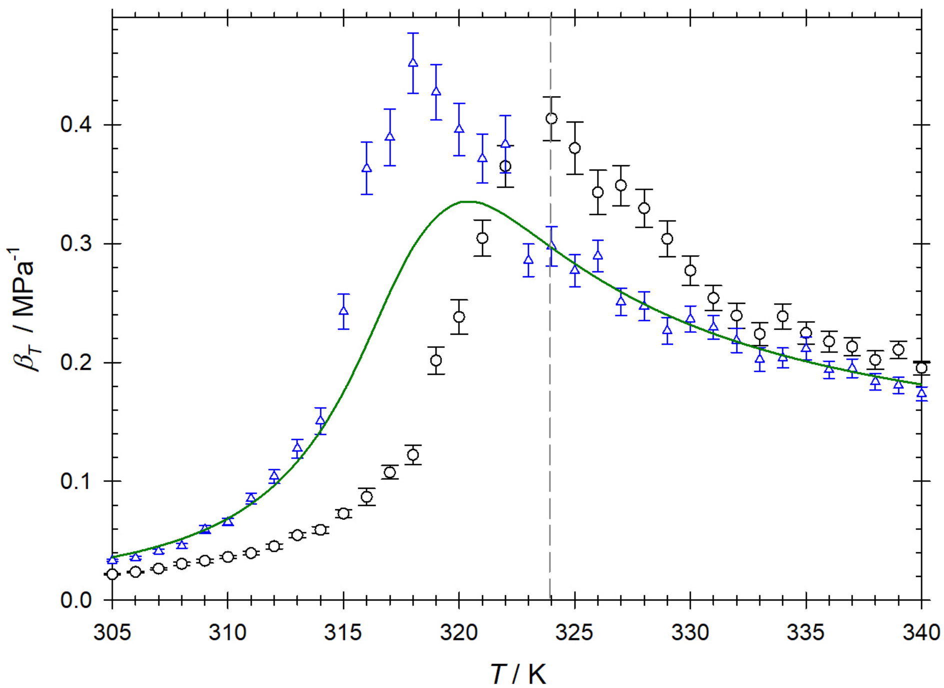

FIG. S4. Isothermal compressibility β_T of CO_2 (blue) and the mixture CO_2 + ethanol (black) along the isobar $p = 10$ MPa. The green line represents the isothermal compressibility of pure CO_2 calculated with the Span-Wagner equation of state [2].

MICROSCOPIC STRUCTURE

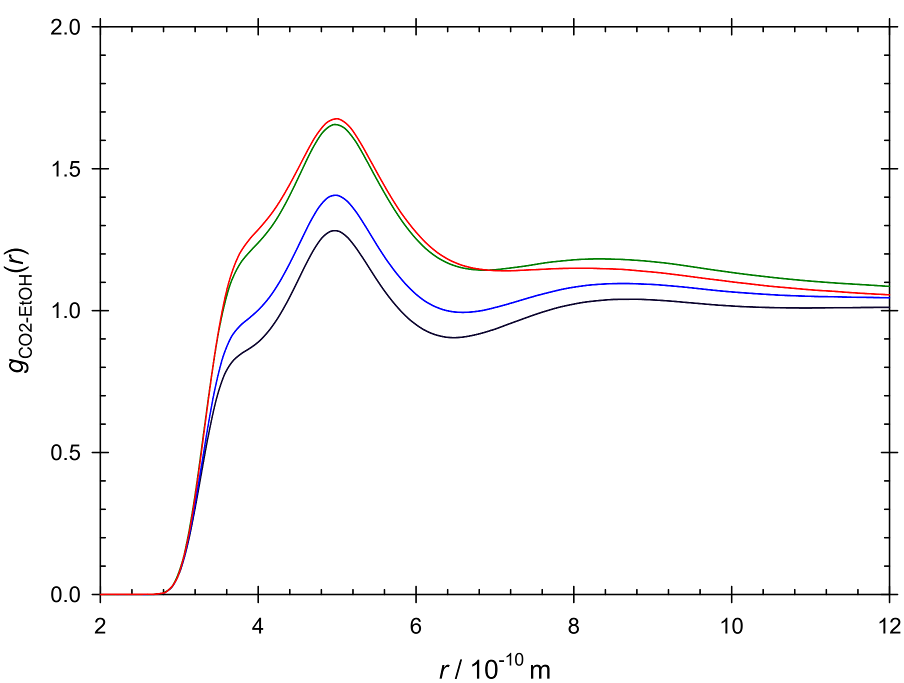

FIG. S5. CO_2-ethanol radial distribution function at $T = 310$ K (black), 320 K (blue), 330 K (green) and 340 K (red) along the isobar $p = 10$ MPa.

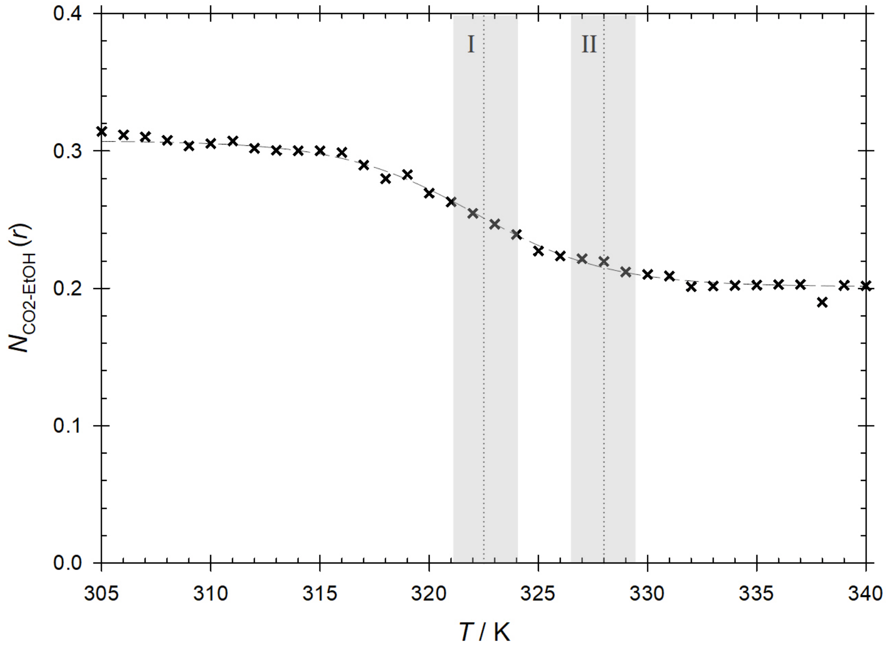

FIG. S6. Average coordination number of the CO_2-ethanol pair along the isobar p = 10 MPa. The dashed line serves as a guide to the eye.

PREDICTIVE EQUATIONS

Several equations were tested on their ability to predict the diffusion coefficient of ethanol infinitely diluted in CO_2. Fig. S7 shows their predictions in comparison with present experimental measurements and molecular dynamics simulation data.

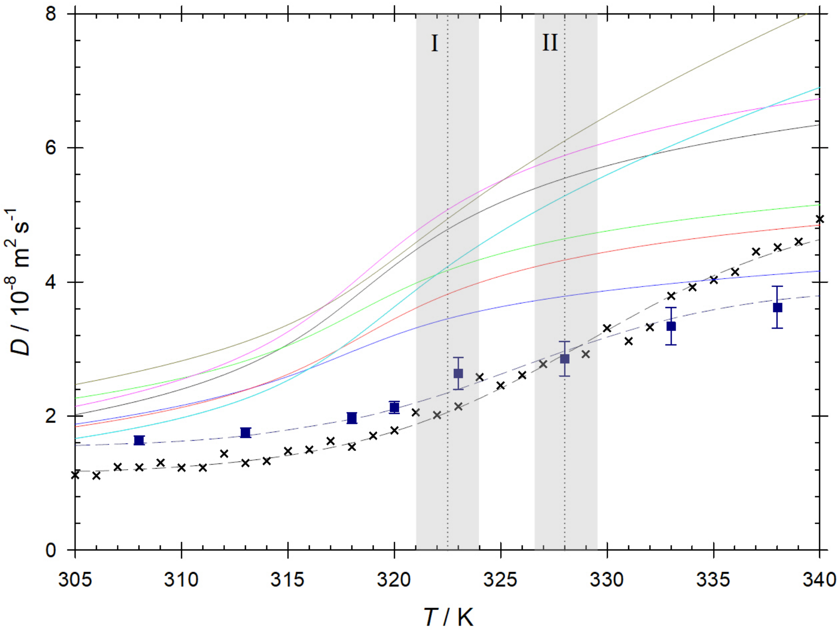

FIG. S7. Fick diffusion coefficient at infinite dilution of the CO_2 + ethanol mixture along the isobar $p = 10$ MPa. Experimental measurements (blue squares) and simulation results (black bullets) are compared with selected predictive equations: Wilke-Chang [3] (black line), Catchpole and King [4] (cyan line), Funazukuri et al. [5] (yellow line), Lai-Tan [6] (green line), He and Yu [7] (blue line), Vaz et al. [8] (red line) and Scheibel [9] (pink line). The dashed lines serve as a guide to the eye.

NUMERICAL SIMULATION RESULTS

TABLE S1. Density ρ, enthalpy h, internal energy u, isobaric heat capacity c_p, isochoric heat capacity c_v, thermal expansion α_v and isothermal compresibility β_T of the CO_2 + ethanol mixture with $x_{CO2} = 0.97$ mol·mol^{-1} along the isobar $p = 10$ MPa. The numbers in parentheses denote the statistical uncertainty in the last digits

T K	ρ mol dm^{-3}	h kJ mol^{-1}	u kJ mol^{-1}	c_p J mol^{-1} K^{-1}	c_v J mol^{-1} K^{-1}	α_v K^{-1}	β_T MPa^{-1}
305	17.6431	-11.363 (1)	-9.392 (1)	103 (4)	15.0 (2)	0.0111 (3)	0.021 (1)
306	17.3900	-11.264 (1)	-9.291 (1)	108 (5)	15.1 (2)	0.0117 (3)	0.024 (1)
307	17.2078	-11.146 (1)	-9.169 (1)	112 (5)	14.8 (2)	0.0128 (4)	0.026 (1)
308	16.9733	-11.038 (2)	-9.063 (2)	110 (5)	15.4 (2)	0.0139 (5)	0.026 (1)
309	16.7440	-10.919 (1)	-8.942 (1)	132 (6)	15.5 (2)	0.0145 (6)	0.034 (2)
310	16.5099	-10.787 (1)	-8.811 (2)	133 (7)	15.5 (2)	0.0154 (5)	0.037 (2)
311	16.2407	-10.658 (1)	-8.683 (1)	134 (6)	15.6 (2)	0.0162 (6)	0.039 (2)
312	15.9789	-10.525 (1)	-8.553 (2)	133 (7)	15.7 (3)	0.0179 (8)	0.043 (3)
313	15.6723	-10.369 (1)	-8.398 (1)	147 (8)	15.7 (2)	0.0204 (7)	0.051 (3)
314	15.3408	-10.209 (1)	-8.242 (2)	163 (8)	17.0 (3)	0.0211 (7)	0.059 (3)
315	15.0566	-10.040 (2)	-8.082 (2)	187 (11)	17.2 (3)	0.0247 (11)	0.076 (5)
316	14.7274	-9.831 (2)	-7.881 (2)	193 (13)	17.4 (3)	0.0278 (13)	0.082 (6)
317	14.1996	-9.639 (2)	-7.701 (2)	263 (17)	18.1 (3)	0.0325 (16)	0.126 (9)
318	13.7597	-9.379 (2)	-7.458 (2)	224 (14)	19.1 (4)	0.0340 (19)	0.116 (8)
319	13.2006	-9.130 (2)	-7.231 (2)	257 (17)	19.3 (4)	0.0509 (26)	0.155 (10)
320	12.4577	-8.838 (2)	-6.967 (2)	406 (32)	20.3 (5)	0.0557 (30)	0.297 (27)
321	11.8604	-8.479 (2)	-6.648 (2)	330 (30)	20.9 (5)	0.0647 (31)	0.263 (28)
322	11.0933	-8.092 (2)	-6.310 (2)	360 (27)	21.6 (6)	0.0714 (35)	0.311 (23)
323	10.3431	-7.676 (2)	-5.953 (2)	363 (32)	22.3 (5)	0.0683 (31)	0.336 (29)
324	9.6679	-7.295 (2)	-5.631 (2)	317 (26)	21.6 (6)	0.0657 (33)	0.337 (26)
325	9.1395	-6.991 (3)	-5.377 (3)	307 (23)	22.3 (7)	0.0560 (34)	0.359 (27)
326	8.6622	-6.671 (3)	-5.115 (3)	305 (26)	21.5 (7)	0.0484 (27)	0.390 (32)
327	8.3640	-6.471 (3)	-4.950 (3)	242 (21)	21.3 (6)	0.0454 (23)	0.318 (28)
328	7.9564	-6.197 (2)	-4.726 (2)	215 (16)	18.7 (5)	0.0406 (20)	0.272 (24)
329	7.7105	-6.031 (2)	-4.592 (2)	197 (16)	19.0 (5)	0.0365 (18)	0.295 (26)
330	7.4506	-5.851 (3)	-4.449 (2)	170 (13)	19.6 (5)	0.0315 (15)	0.299 (20)
331	7.2152	-5.677 (3)	-4.309 (3)	152 (11)	19.5 (6)	0.0283 (12)	0.226 (19)
332	7.0533	-5.545 (3)	-4.208 (3)	136 (13)	18.4 (6)	0.0253 (11)	0.237 (21)
333	6.8707	-5.409 (2)	-4.096 (2)	169 (12)	16.5 (4)	0.0231 (10)	0.330 (24)
334	6.7101	-5.282 (2)	-3.995 (2)	134 (14)	16.7 (5)	0.0236 (11)	0.254 (28)
335	6.5657	-5.175 (2)	-3.912 (2)	101 (9)	16.5 (4)	0.0212 (9)	0.196 (18)
336	6.4372	-5.064 (2)	-3.824 (2)	110 (4)	15.5 (4)	0.0207 (9)	0.218 (9)
337	6.3047	-4.952 (2)	-3.736 (2)	101 (4)	14.9 (3)	0.0195 (7)	0.213 (8)
338	6.2109	-4.881 (2)	-3.682 (2)	96 (4)	14.6 (4)	0.0181 (7)	0.202 (10)
339	6.0860	-4.783 (2)	-3.606 (2)	97 (4)	13.8 (3)	0.0186 (7)	0.210 (8)
340	5.9914	-4.690 (2)	-3.533 (2)	85 (2)	14.5 (5)	0.0166 (5)	0.195 (6)

TABLE S2. Fick diffusion coefficient D, intradiffusion coefficients D_{CO2}, D_{EtOH}, thermodynamic factor Γ and shear viscosity η of the CO_2 + ethanol mixture with $x_{CO2} = 0.97$ mol· mol^{-1} at the given temperature T and pressure p. The numbers in parentheses denote the statistical uncertainty in the last digits.

T K	p MPa	D_{CO2} 10^{-8} m^2 s^{-1}	D_{EtOH} 10^{-8} m^2 s^{-1}	D 10^{-8} m^2 s^{-1}	Γ	η 10^{-4} Pas
305	9.96 (1)	1.947 (2)	1.204 (7)	1.12 (18)	0.452 (8)	1.09 (4)
306	9.96 (1)	1.961 (2)	1.251 (7)	1.11 (19)	0.465 (8)	1.07 (4)
307	9.92 (1)	2.010 (2)	1.292 (7)	1.24 (19)	0.479 (7)	1.00 (4)
308	9.97 (1)	2.062 (2)	1.326 (7)	2.24 (20)	0.485 (8)	1.00 (4)
309	9.95 (1)	2.119 (2)	1.361 (7)	1.31 (20)	0.491 (7)	0.97 (4)
310	9.94 (1)	2.200 (2)	1.398 (8)	1.23 (20)	0.483 (8)	0.86 (3)
311	9.95 (1)	2.260 (2)	1.445 (8)	1.23 (22)	0.487 (8)	0.84 (3)
312	9.97 (1)	2.320 (2)	1.498 (8)	1.44 (24)	0.502 (8)	0.89 (3)
313	9.92 (1)	2.414,(3)	1.527 (9)	1.30 (21)	0.473 (9)	0.83 (3)
314	9.909 (9)	2.509 (3)	1.609 (9)	1.33 (22)	0.499 (9)	0.77 (3)
315	9.954 (9)	2.603 (3)	1.656 (9)	1.48 (24)	0.487 (10)	0.73 (3)
316	9.913 (9)	2.721 (3)	1.745 (9)	1.50 (23)	0.480 (9)	0.74 (3)
317	9.935 (8)	2.845 (3)	1.797 (9)	1.62 (25)	0.500 (9)	0.70 (3)
318	9.918 (8)	3.018 (3)	1.918 (10)	1.54 (25)	0.475 (10)	0.65 (3)
319	9.965 (7)	3.190 (3)	1.990 (10)	1.71 (27)	0.477 (10)	0.67 (2)
320	9.980 (6)	3.407 (3)	2.132 (11)	1.78 (30)	0.481 (8)	0.59 (2)
321	9.990 (6)	3.705 (3)	2.257 (12)	2.05 (31)	0.465 (9)	0.52 (2)
322	9.996 (5)	4.050 (4)	2.438 (14)	2.01 (32)	0.469 (10)	0.47 (2)
323	10.000 (4)	4.447 (4)	2.653 (14)	2.15 (35)	0.447 (10)	0.40 (2)
324	9.998 (3)	4.826 (4)	2.829 (15)	2.58 (40)	0.482 (10)	0.41 (2)
325	10.011 (3)	5.161 (5)	3.060 (16)	2.46 (36)	0.437 (10)	0.37 (2)
326	9.994 (3)	5.548 (5)	3.243 (18)	2.61 (42)	0.437 (10)	0.34 (1)
327	10.024 (3)	5.784 (5)	3.413 (19)	2.78 (42)	0.425 (11)	0.32 (1)
328	9.992 (3)	6.139 (5)	3.653 (20)	2.86 (47)	0.455 (11)	0.31 (1)
329	9.999 (3)	6.359 (5)	3.778 (20)	2.92 (46)	0.441 (13)	0.31 (1)
330	9.999 (3)	6.613 (6)	3.936 (21)	3.31 (50)	0.497 (11)	0.31 (1)
331	9.989 (2)	6.834 (6)	4.099 (22)	3.12 (51)	0.477 (15)	0.32 (1)
332	10.005 (2)	7.065 (6)	4.295 (23)	3.33 (54)	0.489 (14)	0.27 (1)
333	9.999 (2)	7.294 (6)	4.486 (22)	3.79 (58)	0.512 (11)	0.26 (1)
334	9.995 (2)	7.497 (6)	4.654 (25)	3.92 (63)	0.545 (14)	0.27 (1)
335	9.992 (2)	7.664 (6)	4.786 (26)	4.03 (63)	0.523 (13)	0.29 (1)
336	9.999 (2)	7.866 (6)	4.961 (25)	4.15 (64)	0.564 (12)	0.26 (1)
337	9.999 (2)	8.057 (7)	5.147 (26)	4.45 (70)	0.588 (13)	0.26 (1)
338	10.010 (2)	8.185 (7)	5.140 (27)	4.52 (76)	0.599 (10)	0.28 (1)
339	9.998 (2)	8.386 (7)	5.357 (27)	4.60 (76)	0.583 (12)	0.27 (1)
340	10.004 (2)	8.530 (7)	5.521 (27)	4.94 (76)	0.613 (14)	0.27 (1)

TABLE S3. Average coordination number $N_{x-y}(r)$ of the CO_2-CO_2, ethanol-ethanol and CO_2-ethanol pairs for the first coordination shell along the isobar $p = 10$ MPa

T / K	$N_{\mathrm{CO2-CO2}}$ (r)	$N_{\mathrm{EtOH-EtOH}}$ (r)	$N_{\mathrm{CO2-CO2}}$ (r)
305	9.50	1.42	0.314
306	9.47	1.38	0.312
307	9.50	1.35	0.310
308	9.48	1.33	0.308
309	9.49	1.31	0.304
310	9.32	1.30	0.306
311	9.13	1.27	0.307
312	9.04	1.26	0.302
313	9.06	1.25	0.301
314	8.90	1.24	0.300
315	8.65	1.23	0.300
316	8.73	1.24	0.299
317	8.22	1.19	0.290
318	8.31	1.22	0.280
319	7.97	1.19	0.283
320	7.82	1.14	0.269
321	7.53	1.18	0.263
322	7.17	1.14	0.255
323	6.84	1.16	0.247
324	6.50	1.09	0.240
325	6.13	1.14	0.228
326	6.21	1.12	0.224
327	5.85	1.11	0.222
328	5.87	1.07	0.220
329	5.52	1.06	0.212
330	5.42	0.979	0.210
331	5.53	0.981	0.209
332	5.28	0.938	0.201
333	5.18	0.891	0.202
334	5.16	0.836	0.202
335	5.04	0.837	0.202
336	5.11	0.795	0.203
337	4.84	0.757	0.203
338	4.84	0.768	0.190
339	4.83	0.747	0.202
340	4.83	0.726	0.202

[1] G. Rutkai, A. Köster, G. Guevara-Carrion, T. Janzen, M. Schappals, C. W. Glass, M. Bernreuther, A. Wafai, S. Stephan, M. Kohns, S. Reiser, S. Deublein, M. Horsch, H. Hasse, and J. Vrabec, Comput. Phys. Commun. **221**, 343 (2017).

[2] R. Span and W. Wagner, J. Phys. Chem. Ref. Data **25**, 1509 (1996).

[3] C. R. Wilke and P. Chang, AIChE J. **1**, 264 (1955).

[4] O. J. Catchpole and M. B. King, Ind. Eng. Chem. Res. **33**, 1828 (1994).

[5] T. Funazukuri, C. Y. Kong, and S. Kagei, Ind. End. Chem. Res. **39**, 835 (2000).

[6] C.-C. Lai and C.-S. Tan, Ind. Eng. Chem. Res. **34**, 674 (1995).

[7] C.-H. He and Y.-S. Yu, Ind. Eng. Chem. Res. **37**, 3793 (1998).

[8] R. V. Vaz, A. L. Magalhaes, and C. M. Silva, J. Supercrit. Fluids **91**, 24 (2014).

[9] E. G. Scheibel, Ind. Eng. Chem. **46**, 2007 (1954).