Liquid Densities of γ-Butyrolactone and *N*-Methyl-2-pyrrolidone from 273 to 473 K and at Pressures up to 40 MPa

E. Christian Ihmels and Jürgen Gmehling*

Carl von Ossietzky University of Oldenburg, Department of Industrial Chemistry, P.O. Box 2503, D-26111 Oldenburg, Germany

Densities of γ-butyrolactone and *N*-methyl-2-pyrrolidone (NMP) have been measured with a computer-controlled high-temperature, high-pressure vibrating tube densimeter system (DMA-HDT) in the liquid state. The uncertainty in density measurement was estimated to be less than ±0.2 $kg\cdot m^{-3}$. The densities were measured for temperatures from 273 K to 473 K and pressures from 0.3 MPa up to 40 MPa, whereby a density range between (947 and 1168) $kg\cdot m^{-3}$ for γ-butyrolactone (353 data points) and between (865 and 1068) $kg\cdot m^{-3}$ for NMP (370 data points) was covered. The experimental data were correlated with the three-dimensional density correlation system (TRIDEN) and compared with published data.

Introduction

The main use of γ-butyrolactone is as an intermediate in the synthesis of *N*-methyl-2-pyrrolidone (NMP), pyrrolidone, herbicides, growth regulators, α-acetobutyrolactone (a vitamin B_1 intermediate), and the rubber additive thiodibutyric acid. Furthermore, γ-butyrolactone is used as a solvent for polymers, as a polymerization catalyst, in hair wave compositions, in suntan lotions, and in pharmaceuticals. It is also used in printing inks, for example, for ink-jet printing, as an extractant in the petroleum industry, as a stabilizer for chlorohydrocarbons and phosphorus-based pesticides, and as a nematocide.

Large-scale production of NMP is predominantly carried out by reacting γ-butyrolactone with methylamine. Because of its low volatility, thermal stability, high polarity, and aprotic, noncorrosive properties, NMP is an important solvent. Its auspicious toxicological and ecological properties account for the fact that NMP is replacing other solvents such as chlorinated hydrocarbons. NMP is used in many industrial fields, for example, for extraction of aromatics in petrochemical processing, for removal of CO_2 and H_2S in gas purifications, as an entrainer for extractive distillation processes, as a reaction medium for the production of polymers, and as a cleaning agent for silicon wafers.

Compressed liquid densities of NMP and γ-butyrolactone were measured with a computer-controlled vibrating tube densimeter. The densimeter had been calibrated with degassed water and butane and vacuum measurements. Densities were measured for temperatures from 273 K to 473 K and pressures from 0.3 MPa up to 40 MPa, whereby a density range between (947 and 1168) $kg\cdot m^{-3}$ for γ-butyrolactone (353 data points) and between (865 and 1068) $kg\cdot m^{-3}$ for NMP (370 data points) was covered. The measured densities of NMP and γ-butyrolactone were correlated with the three-dimensional correlating model TRIDEN. Details of the measurement system, the calibration, and the correlation are described by Ihmels and Gmehling.[1,2]

* To whom correspondence should be addressed. E-mail: gmehling@tech.chem.uni-oldenburg.de. Telephone: ++49-441-798-3831. Fax: ++49-441-798-3330.

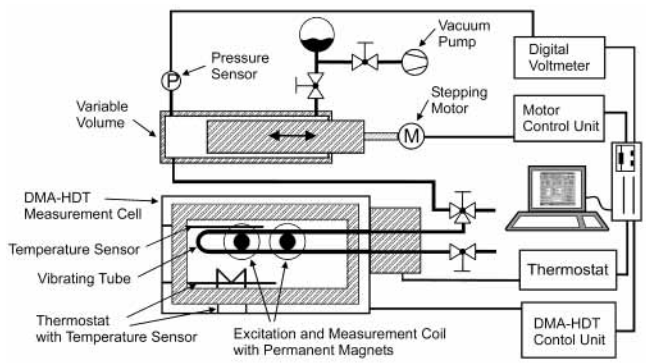

Figure 1. Schematic diagram of the computer-controlled density measurement unit.

Experimental Section

γ-Butyrolactone ($C_4H_6O_2$, M = 86.09 $g\cdot mol^{-1}$, CAS-RN 96-48-0) and *N*-methylpyrrolidone (NMP, C_5H_9NO, M = 99.13 $g\cdot mol^{-1}$, CAS-RN 872-50-4) were obtained from Acros and Riedel-de Haën, respectively. Both components were stored over a 3 Å molecular sieve and degassed by distillation. The final purities were checked by gas chromatography (γ-butyrolactone, >99.9 mass %; NMP, >99.98 mass %) and by Karl Fischer titration (water content of NMP < 20 ppm).

A computer-operated vibrating tube densimeter system for high temperatures and pressures (for temperatures from 273 to 623 K and pressures up to 40 MPa) was used for the measurement of the density data for γ-butyrolactone and NMP. The automated equipment can be used for the determination of densities in the sub- and supercritical states. With this apparatus, a large number of data points can be obtained in a rather short time with a minimum of manual effort. A temperature and pressure program can be driven to obtain a complete $P\rho T$ surface for the desired

10.1021/je0255877 CCC: $22.00
Published on Web 10/17/2002

Table 1. Experimental Densities of γ-Butyrolactone

T/K	P/MPa	ρ/kg·m^{-3}	T/K	P/MPa	ρ/kg·m^{-3}	T/K	P/MPa	ρ/kg·m^{-3}	T/K	P/MPa	ρ/kg·m^{-3}
273.21	0.258	1148.78	313.16	20.001	1121.10	353.14	39.916	1096.76	398.13	19.962	1042.20
273.21	5.034	1151.16	313.16	24.995	1123.87	358.14	0.349	1065.52	398.13	24.990	1046.17
273.21	9.993	1153.64	313.16	29.998	1126.58	358.14	5.006	1068.95	398.13	30.012	1050.00
273.21	15.001	1156.06	313.16	35.004	1129.30	358.14	10.005	1072.54	398.13	34.963	1053.77
273.21	20.006	1158.46	313.16	39.957	1131.94	358.14	15.004	1076.03	403.12	0.352	1020.43
273.21	24.990	1160.83	318.16	0.346	1104.81	358.14	19.985	1079.42	403.12	4.965	1024.67
273.21	30.004	1163.17	318.16	4.965	1107.64	358.14	24.980	1082.76	403.12	9.956	1029.09
273.21	35.003	1165.47	318.16	9.991	1110.66	358.14	30.015	1086.03	403.13	14.958	1033.37
273.21	39.973	1167.75	318.16	14.996	1113.60	358.14	34.979	1089.25	403.12	19.991	1037.55
278.21	0.322	1143.92	318.16	19.981	1116.47	358.14	39.928	1092.37	403.13	24.985	1041.57
278.21	5.023	1146.33	318.16	25.008	1119.32	363.14	0.335	1060.55	403.13	29.987	1045.51
278.21	9.963	1148.83	318.16	30.014	1122.11	363.14	4.979	1064.06	403.12	35.009	1049.32
278.21	14.992	1151.32	318.16	35.000	1124.84	363.14	9.965	1067.72	408.12	0.361	1015.34
278.21	19.985	1153.77	318.16	39.946	1127.53	363.14	14.997	1071.32	408.12	5.031	1019.75
278.21	24.970	1156.17	323.15	0.334	1099.91	363.14	20.013	1074.80	408.12	9.976	1024.24
278.21	29.994	1158.56	323.15	4.975	1102.82	363.14	24.978	1078.19	408.13	15.001	1028.64
278.21	35.020	1160.91	323.15	9.982	1105.89	363.14	29.996	1081.55	408.12	19.994	1032.85
278.21	39.992	1163.24	323.15	14.973	1108.89	363.14	34.973	1084.81	408.12	24.974	1036.97
283.21	0.325	1139.03	323.15	19.966	1111.82	363.14	39.929	1088.01	408.12	30.026	1040.99
283.21	4.986	1141.47	323.15	24.963	1114.72	368.13	0.335	1055.59	408.12	34.988	1044.87
283.21	10.020	1144.07	323.15	29.995	1117.58	368.14	5.038	1059.23	413.12	0.365	1010.23
283.21	15.011	1146.60	323.15	35.002	1120.38	368.14	10.002	1062.95	413.12	4.958	1014.67
283.21	19.978	1149.08	323.15	39.950	1123.12	368.13	14.957	1066.57	413.12	9.982	1019.36
283.21	24.994	1151.56	328.15	0.338	1095.02	368.14	20.009	1070.16	413.12	14.981	1023.84
283.21	29.989	1153.98	328.15	4.971	1097.99	368.14	24.993	1073.64	413.12	19.982	1028.17
283.21	34.998	1156.39	328.15	10.028	1101.16	368.14	29.974	1077.02	413.12	24.975	1032.35
283.21	40.024	1158.73	328.15	14.977	1104.20	368.14	34.988	1080.37	413.12	30.005	1036.47
288.21	0.349	1134.14	328.15	19.960	1107.19	368.14	39.933	1083.62	413.13	34.989	1040.43
288.21	4.992	1136.63	328.15	24.972	1110.15	373.13	0.340	1050.62	418.12	0.344	1005.07
288.21	10.033	1139.29	328.15	30.009	1113.06	373.13	4.977	1054.29	418.12	5.020	1009.72
288.21	15.026	1141.87	328.15	35.005	1115.92	373.14	9.979	1058.13	418.12	9.982	1014.44
288.21	19.984	1144.41	328.15	39.933	1118.71	373.13	14.995	1061.87	418.12	14.971	1019.03
288.21	24.999	1146.92	333.15	0.347	1090.13	373.14	19.982	1065.50	418.12	19.967	1023.46
288.21	29.971	1149.38	333.15	4.998	1093.18	373.14	24.979	1069.06	418.12	24.973	1027.74
288.21	34.982	1151.84	333.15	9.965	1096.37	373.13	29.975	1072.51	418.12	30.012	1031.97
288.21	39.996	1154.25	333.15	14.972	1099.50	373.13	35.033	1075.92	418.12	34.977	1036.00
293.21	0.337	1129.24	333.15	19.973	1102.56	373.13	39.927	1079.25	423.12	0.353	999.92
293.21	4.997	1131.80	333.15	25.006	1105.60	378.13	0.340	1045.62	423.12	5.007	1004.66
293.21	10.010	1134.50	333.15	30.013	1108.56	378.13	4.951	1049.36	423.12	9.969	1009.52
293.22	15.032	1137.15	333.15	35.002	1111.47	378.13	9.993	1053.33	423.12	14.973	1014.22
293.21	20.033	1139.73	333.15	39.935	1114.31	378.13	14.955	1057.12	423.12	19.965	1018.75
293.21	24.995	1142.31	338.15	0.349	1085.23	378.13	19.980	1060.86	423.12	24.972	1023.14
293.21	29.982	1144.80	338.15	5.010	1088.35	378.13	25.010	1064.47	423.12	29.976	1027.41
293.22	34.978	1147.31	338.15	9.962	1091.60	378.13	29.983	1068.03	423.12	34.978	1031.55
293.21	39.990	1149.77	338.15	14.955	1094.80	378.13	34.975	1071.52	428.12	0.375	994.75
298.22	0.337	1124.35	338.15	19.990	1097.96	378.13	39.930	1074.88	428.12	5.008	999.61
298.22	4.985	1126.95	338.15	25.024	1101.02	383.13	0.343	1040.62	428.12	10.025	1004.64
298.22	10.001	1129.71	338.15	29.986	1104.06	383.13	4.963	1044.46	428.12	14.981	1009.41
298.21	14.996	1132.42	338.15	35.014	1107.00	383.13	10.011	1048.52	428.12	19.965	1014.03
298.22	19.975	1135.05	338.15	39.954	1109.91	383.13	14.983	1052.40	428.12	24.977	1018.52
298.22	24.997	1137.68	343.14	0.344	1080.31	383.13	19.963	1056.19	428.12	29.997	1022.91
298.22	29.987	1140.26	343.14	5.015	1083.51	383.13	24.977	1059.89	428.12	34.990	1027.10
298.22	35.003	1142.81	343.14	9.998	1086.86	383.13	30.017	1063.52	433.12	0.378	989.55
298.22	39.965	1145.32	343.14	14.981	1090.12	383.13	35.037	1067.04	433.12	5.030	994.55
303.22	0.340	1119.46	343.14	20.006	1093.33	383.13	39.922	1070.51	433.12	9.962	999.63
303.22	5.023	1122.14	343.14	24.983	1096.47	388.13	0.332	1035.58	433.12	14.978	1004.58
303.22	10.000	1124.94	343.14	30.003	1099.55	388.13	4.983	1039.55	433.12	19.980	1009.32
303.22	15.022	1127.71	343.14	34.995	1102.57	388.13	9.955	1043.65	433.12	24.973	1013.89
303.22	19.964	1130.39	343.14	39.924	1105.52	388.13	14.983	1047.65	433.12	29.984	1018.34
303.22	24.975	1133.07	348.14	0.340	1075.38	388.13	19.962	1051.53	433.12	34.970	1022.65
303.22	29.986	1135.71	348.14	4.974	1078.64	388.13	24.960	1055.31	438.12	0.372	984.30
303.22	34.995	1138.31	348.14	10.003	1082.09	388.13	30.002	1059.01	438.12	4.991	989.41
303.22	39.980	1140.86	348.14	14.970	1085.41	388.13	35.014	1062.63	438.12	9.978	994.68
308.22	0.338	1114.57	348.14	19.963	1088.67	388.13	39.923	1066.13	438.12	15.016	999.77
308.22	4.963	1117.28	348.14	24.978	1091.87	393.13	0.345	1030.56	438.12	19.999	1004.60
308.22	9.967	1120.16	348.14	30.003	1095.05	393.13	5.005	1034.62	438.12	24.977	1009.27
308.22	14.974	1122.98	348.14	35.006	1098.12	393.13	9.974	1038.82	438.12	29.991	1013.81
308.22	19.989	1125.75	348.14	39.939	1101.13	393.13	14.998	1042.93	438.12	34.991	1018.19
308.22	24.983	1128.48	353.14	0.351	1070.46	393.13	19.990	1046.89	438.12	39.748	1022.45
308.22	29.986	1131.16	353.14	5.026	1073.82	393.13	25.008	1050.73	443.12	0.381	979.05
308.22	35.029	1133.82	353.14	9.967	1077.29	393.13	29.986	1054.51	443.12	4.967	984.26
308.22	39.982	1136.40	353.14	14.985	1080.72	393.13	34.981	1058.21	443.12	9.974	989.69
313.16	0.324	1109.67	353.14	19.979	1084.06	398.13	0.359	1025.51	443.12	14.973	994.86
313.16	5.016	1112.48	353.14	24.978	1087.31	398.13	4.971	1029.64	443.12	19.973	999.83
313.16	9.965	1115.38	353.14	30.005	1090.52	398.13	9.978	1033.98	443.12	24.989	1004.64
313.16	15.015	1118.29	353.14	35.006	1093.68	398.13	14.985	1038.16	443.12	29.998	1009.26

Table 1 (Continued)

T/K	P/MPa	ρ/kg·m^{-3}	T/K	P/MPa	ρ/kg·m^{-3}	T/K	P/MPa	ρ/kg·m^{-3}	T/K	P/MPa	ρ/kg·m^{-3}
443.12	34.994	1013.74	453.12	19.976	990.31	463.12	0.416	957.71	468.12	19.964	975.92
448.12	0.367	973.73	453.12	24.978	995.30	463.12	4.988	963.55	468.12	24.976	981.28
448.12	4.981	979.13	453.12	30.002	1000.18	463.12	9.957	969.54	468.11	29.977	986.44
448.12	9.996	984.71	453.12	34.986	1004.80	463.12	14.994	975.30	468.12	34.980	991.39
448.12	15.002	990.02	458.12	0.409	963.10	463.12	20.003	980.77	473.12	0.415	946.83
448.12	19.980	995.08	458.12	4.974	968.75	463.12	24.978	985.96	473.12	4.985	953.01
448.12	25.010	999.97	458.12	9.959	974.61	463.12	29.955	990.97	473.12	9.982	959.38
448.12	29.989	1004.72	458.12	14.976	980.20	463.12	34.990	995.87	473.11	14.991	965.42
448.12	34.996	1009.28	458.12	19.967	985.52	468.12	0.428	952.30	473.11	19.974	971.12
453.12	0.382	968.42	458.12	25.003	990.62	468.12	5.004	958.31	473.12	24.976	976.59
453.12	4.976	973.95	458.12	30.003	995.58	468.12	10.014	964.52	473.12	30.002	981.86
453.12	9.981	979.67	458.12	34.956	1000.35	468.12	14.979	970.35	473.12	34.992	986.92
453.12	14.960	985.09									

component. The measurement system was developed in the thesis of Ihmels.[3] Densities as a function of temperature and pressure of several liquids and liquefied gases (e.g., toluene, carbon dioxide, carbonyl sulfide, hydrogen sulfide, sulfur hexafluoride, dinitrogen monoxide, R227ea, sulfur dioxide, MTBE, ETBE, DIPE, 1-butanol, and DIPE/1-butanol mixtures) have already been published.[1−7] The comparisons with reference equations of state (EoS) for toluene, CO_2, and SF_6 demonstrated the high accuracy and suitability of this measurement system. Using the measured densities of sulfur dioxide, a new Helmholtz-type equation of state was developed by Ihmels et al.[7]

The apparatus and procedure of the measurements are described in detail by Ihmels and Gmehling.[1,2] A scheme of the density measurement system is shown in Figure 1. A prototype of a high-pressure, high-temperature vibrating tube densimeter (DMA-HDT) from "Labor für Meβtechnik Dr. Hans Stabinger" (Graz, Austria) is the essential part of the experimental setup. The temperature is measured using a Pt100 resistance thermometer, and the pressure is monitored by means of a calibrated external pressure sensor (model PDCR 911, pressure range 60 MPa, Druck). The density values are obtained from the periods of oscillation of the vibrating tube. For the calibration, the period of oscillation at zero pressure and the two reference substances water and butane were used. The reference densities were calculated using the reference EoS from Wagner and Pruss[8,9] for water and the EoS from Younglove and Ely[10] for butane. The uncertainty of the temperature is estimated to be ±0.03 K, and the pressure has an estimated uncertainty of ±6 kPa. For density measurements in the temperature and pressure ranges covered (273 K to 473 K, 0.3 MPa to 40 MPa) a maximum error of ±0.2 kg·m^{-3} is obtained.

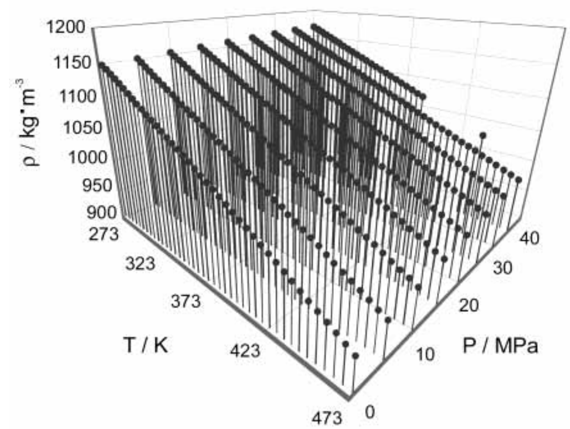

Figure 2. Densities of γ-butyrolactone at temperatures between 273 K and 473 K and pressures between 0.3 and 40 MPa.

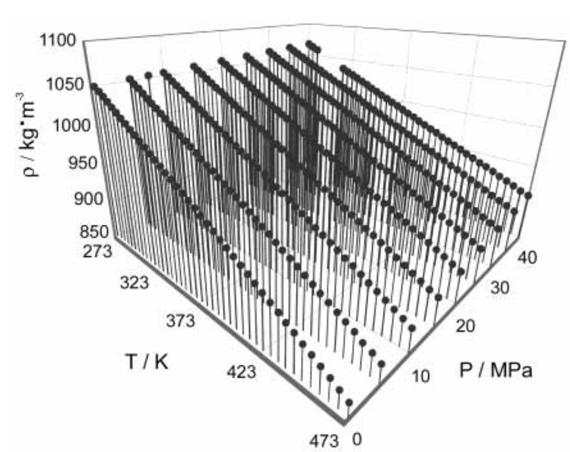

Figure 3. Densities of NMP at temperatures between 273 K and 473 K and pressures between 0.3 and 40 MPa.

Results and Discussion

In this work, the densities of γ-butyrolactone (353 data points) and NMP (370 data points) in the compressed liquid state were measured from 273 K to 473 K and from 0.3 MPa up to 40 MPa. The results are listed in Tables 1 and 2 and presented graphically in Figures 2 and 3.

Aside from several published[11] density measurements at atmospheric or saturation pressure for γ-butyrolactone up to 553 K and NMP up to 373 K, compressed liquid densities were measured only for γ-butyrolactone at 293 K and up to 10 MPa by Fornefeld-Schwarz et al.[12] Therefore, these new measurements represent a wide extension of the $P\rho T$ data for γ-butyrolactone and NMP.

The measured densities were correlated with the three-dimensional $P\rho T$-correlating model TRIDEN.[1−3] In this model the Tait equation for isothermal compressed densities was combined with a modified Rackett equation for the liquid saturation densities and the Wagner vapor pressure equation in the "2.5,5" form, used as a reference state (ρ_0 and P_0), which is required for the Tait equation. Using these equations, it is possible to correlate the $P\rho T$ data in the whole liquid state up to the critical point, nearly within experimental error. The TRIDEN model is also applicable for correlations of mixture densities and the calculation of excess volumes.[6] In this work only densities up to the vicinity of the normal boiling points were measured. Therefore, the Wagner vapor pressure equation was omitted and 0.1013 MPa was used as a fixed reference pressure for all temperatures. The reference densities ρ_0 at $P_0 = 0.1013$ MPa were extrapolated from the compressed

Table 2. Experimental Densities of *N*-Methyl-2-pyrrolidone (NMP)

T/K	P/MPa	ρ/kg·m^{-3}	T/K	P/MPa	ρ/kg·m^{-3}	T/K	P/MPa	ρ/kg·m^{-3}	T/K	P/MPa	ρ/kg·m^{-3}
273.25	0.259	1049.53	313.16	15.006	1022.12	353.13	35.003	1000.50	398.11	9.996	945.57
273.25	4.990	1051.84	313.15	19.985	1024.83	353.13	39.985	1003.37	398.11	14.983	949.62
273.25	9.977	1054.24	313.16	25.025	1027.50	358.13	0.295	973.63	398.11	20.005	953.59
273.25	14.980	1056.59	313.15	30.010	1030.08	358.13	4.964	977.01	398.11	25.020	957.40
273.25	19.988	1058.91	313.15	34.984	1032.59	358.13	9.989	980.51	398.11	29.967	961.01
273.25	25.005	1061.18	313.15	39.977	1035.09	358.13	14.989	983.91	398.11	34.967	964.56
273.25	7.678	1052.99	318.15	0.330	1009.36	358.13	20.019	987.21	398.11	39.987	968.01
273.25	4.980	1051.82	318.15	4.969	1012.13	358.13	25.005	990.39	403.11	0.347	932.55
273.25	9.968	1054.21	318.16	9.960	1015.03	358.12	29.994	993.48	403.11	5.018	936.81
273.25	15.016	1056.58	318.15	14.983	1017.88	358.12	34.993	996.50	403.11	9.981	941.14
273.25	19.973	1058.88	318.15	19.987	1020.65	358.12	39.998	999.44	403.11	14.981	945.33
273.25	25.003	1061.16	318.15	24.967	1023.34	363.12	0.308	969.13	403.11	19.975	949.34
273.25	30.008	1063.39	318.15	30.000	1026.00	363.12	4.977	972.59	403.11	24.988	953.23
273.25	34.991	1065.57	318.15	35.022	1028.59	363.12	9.968	976.17	403.11	29.990	956.95
273.25	39.983	1067.71	318.15	39.962	1031.10	363.12	14.999	979.66	403.11	34.987	960.58
278.25	0.344	1045.07	323.15	0.337	1004.94	363.12	20.004	983.02	403.11	40.008	964.10
278.25	4.966	1047.38	323.15	4.985	1007.77	363.12	25.016	986.28	408.10	0.349	927.89
278.25	10.027	1049.86	323.15	9.970	1010.74	363.12	30.006	989.44	408.10	4.972	932.22
278.25	14.971	1052.23	323.15	14.987	1013.65	363.12	34.998	992.51	408.10	10.004	936.73
278.25	20.007	1054.59	323.15	20.008	1016.48	363.12	39.956	995.48	408.10	14.987	941.01
278.25	25.024	1056.93	323.15	24.987	1019.22	368.12	0.311	964.62	408.10	20.016	945.15
278.25	30.022	1059.19	323.15	29.998	1021.92	368.12	4.986	968.16	408.10	24.999	949.09
278.25	34.975	1061.40	323.15	34.961	1024.53	368.12	9.992	971.84	408.10	30.010	952.92
278.25	39.960	1063.60	323.15	39.997	1027.13	368.12	15.027	975.41	408.10	35.004	956.61
283.25	0.331	1040.59	328.15	0.339	1000.50	368.12	19.962	978.80	408.10	40.003	960.18
283.25	5.030	1042.98	328.15	4.953	1003.38	368.12	25.028	982.15	413.10	0.365	923.24
283.25	10.021	1045.49	328.15	10.013	1006.46	368.12	30.025	985.39	413.10	4.975	927.67
283.25	14.976	1047.91	328.15	14.959	1009.39	368.12	35.007	988.52	413.10	9.959	932.25
283.25	20.005	1050.33	328.15	19.987	1012.29	368.12	39.976	991.56	413.10	14.985	936.67
283.25	25.029	1052.69	328.15	24.979	1015.09	373.11	0.349	960.11	413.10	20.022	940.92
283.25	30.004	1054.99	328.15	30.012	1017.86	373.12	5.005	963.73	413.10	24.972	944.93
283.25	34.973	1057.25	328.15	35.013	1020.54	373.12	10.010	967.50	413.10	30.007	948.86
283.25	39.991	1059.49	328.15	39.999	1023.15	373.12	15.005	971.13	413.10	34.994	952.61
288.25	0.336	1036.12	333.14	0.335	996.05	373.12	19.985	974.62	413.10	39.972	956.24
288.25	5.001	1038.55	333.14	4.995	999.03	373.12	25.007	978.03	418.10	0.325	918.50
288.25	10.027	1041.12	333.14	9.982	1002.13	373.12	29.992	981.32	418.10	4.990	923.12
288.25	14.966	1043.59	333.14	15.009	1005.17	373.12	34.971	984.50	418.10	9.972	927.81
288.25	19.997	1046.06	333.14	19.983	1008.11	373.12	40.007	987.62	418.10	15.006	932.34
288.25	25.028	1048.47	333.14	25.019	1011.00	378.11	0.341	955.55	418.10	19.980	936.64
288.25	30.005	1050.81	333.14	30.016	1013.80	378.12	5.024	959.29	418.10	24.999	940.81
288.26	34.982	1053.11	333.14	34.995	1016.51	378.11	10.021	963.15	418.10	30.005	944.79
293.25	0.333	1031.65	333.14	39.978	1019.17	378.12	14.977	966.83	418.10	35.006	948.64
293.26	4.970	1034.12	338.14	0.335	991.59	378.11	20.011	970.44	418.10	39.982	952.34
293.26	10.025	1036.74	338.14	4.956	994.62	378.11	25.018	973.92	423.10	0.306	913.75
293.26	14.970	1039.27	338.14	10.020	997.85	378.11	30.039	977.28	423.10	5.021	918.55
293.26	20.005	1041.79	338.14	14.971	1000.91	378.12	35.018	980.54	423.10	9.980	923.36
293.26	25.030	1044.25	338.14	19.993	1003.93	378.12	40.003	983.70	423.10	14.989	927.98
293.26	30.021	1046.64	338.14	24.980	1006.85	383.11	0.340	950.98	423.10	20.001	932.41
293.26	34.993	1048.99	338.14	30.023	1009.73	383.11	4.990	954.79	423.10	24.995	936.65
298.26	0.308	1027.16	338.14	35.013	1012.51	383.11	9.991	958.74	423.10	30.024	940.74
298.26	4.980	1029.71	338.14	40.015	1015.21	383.11	15.020	962.57	423.10	35.027	944.65
298.26	10.022	1032.39	343.14	0.330	987.12	383.11	19.972	966.21	423.10	40.013	948.44
298.26	14.961	1034.96	343.14	5.006	990.26	383.11	25.023	969.79	428.09	0.356	909.07
298.26	20.009	1037.53	343.14	9.989	993.51	383.11	30.036	973.23	428.10	4.980	913.91
298.26	25.031	1040.04	343.14	15.020	996.69	383.11	35.010	976.55	428.10	9.993	918.89
298.26	30.023	1042.48	343.14	19.962	999.73	383.11	39.996	979.77	428.10	14.978	923.62
298.26	34.964	1044.85	343.14	24.977	1002.73	388.11	0.341	946.40	428.10	20.012	928.18
303.26	0.323	1022.70	343.14	29.979	1005.64	388.11	4.981	950.31	428.10	25.000	932.50
303.26	5.004	1025.31	343.14	35.020	1008.51	388.11	9.973	954.35	428.09	30.006	936.68
303.26	10.026	1028.05	343.14	39.991	1011.27	388.11	14.999	958.26	428.10	35.028	940.67
303.26	15.028	1030.71	348.13	0.301	982.62	388.11	20.030	962.04	428.10	39.997	944.54
303.26	20.010	1033.30	348.13	4.961	985.83	388.11	25.003	965.65	433.09	0.362	904.31
303.26	25.022	1035.85	348.13	10.005	989.18	388.11	29.956	969.12	433.09	5.008	909.28
303.26	30.010	1038.34	348.13	14.985	992.42	388.11	34.984	972.54	433.09	9.991	914.39
303.26	35.002	1040.77	348.13	20.017	995.58	388.11	39.983	975.84	433.09	14.974	919.24
308.26	0.326	1018.25	348.13	25.008	998.63	393.11	0.337	941.80	433.09	20.001	923.91
308.27	5.009	1020.92	348.13	29.987	1001.59	393.11	4.991	945.82	433.09	24.992	928.34
308.26	10.003	1023.71	348.13	34.999	1004.49	393.11	10.004	949.98	433.09	29.987	932.57
308.27	15.020	1026.43	348.13	40.000	1007.32	393.11	14.958	953.93	433.09	35.017	936.71
308.27	20.005	1029.08	353.13	0.305	978.14	393.11	19.981	957.79	433.09	40.003	940.65
308.27	25.025	1031.68	353.13	4.969	981.43	393.11	25.011	961.52	438.09	0.334	899.49
308.26	29.987	1034.21	353.13	9.999	984.86	393.11	29.963	965.07	438.09	4.959	904.62
308.26	35.026	1036.69	353.13	15.000	988.18	393.11	34.985	968.56	438.09	9.994	909.91
313.15	0.328	1013.79	353.13	20.002	991.39	393.11	39.988	971.92	438.09	14.981	914.87
313.15	4.985	1016.50	353.13	25.014	994.51	398.11	0.346	937.19	438.09	20.023	919.67
313.15	10.011	1019.36	353.13	30.010	997.55	398.11	4.983	941.30	438.09	25.014	924.20

Table 2 (Continued)

T/K	P/MPa	ρ/kg·m^{-3}	T/K	P/MPa	ρ/kg·m^{-3}	T/K	P/MPa	ρ/kg·m^{-3}	T/K	P/MPa	ρ/kg·m^{-3}
438.09	30.004	928.54	448.09	25.004	915.85	458.09	19.989	902.49	468.09	10.022	882.56
438.09	35.004	932.72	448.09	29.993	920.38	458.09	24.979	907.46	468.08	14.961	888.32
438.09	40.005	936.75	448.09	34.986	924.74	458.09	30.022	912.26	468.09	19.989	893.86
443.09	0.392	894.74	448.09	40.015	928.97	458.09	35.006	916.79	468.09	25.028	899.13
443.09	5.006	899.98	453.09	0.393	885.03	458.09	39.998	921.12	468.08	29.966	904.05
443.09	9.985	905.38	453.09	5.028	890.63	463.09	0.416	875.19	468.09	35.003	908.83
443.09	15.012	910.52	453.09	9.984	896.29	463.09	4.954	881.04	468.08	39.969	913.34
443.09	19.977	915.35	453.09	15.028	901.72	463.09	10.005	887.11	473.08	0.431	865.24
443.09	24.982	920.00	453.09	20.025	906.83	463.09	14.984	892.80	473.08	4.995	871.49
443.09	30.008	924.48	453.09	24.958	911.62	463.09	19.985	898.17	473.08	9.982	877.88
443.09	35.018	928.75	453.09	30.022	916.33	463.09	24.969	903.26	473.08	15.006	883.90
443.09	39.986	932.83	453.09	34.965	920.74	463.09	29.990	908.15	473.08	19.980	889.52
448.09	0.360	889.86	453.09	39.978	925.02	463.09	35.028	912.83	473.08	24.975	894.87
448.09	5.009	895.32	458.09	0.406	880.13	463.09	39.978	917.24	473.08	29.975	899.96
448.09	9.959	900.81	458.09	5.033	885.88	468.09	0.423	870.23	473.08	34.999	904.84
448.09	14.962	906.07	458.09	10.016	891.75	468.08	5.017	876.34	473.08	40.018	909.50
448.09	20.008	911.10	458.09	14.959	897.21						

liquid density measurements and correlated with the modified Rackett eq 1:

$$\rho_0 = A_R/B_R^{[1+(1-T/C_R)^D R]} \tag{1}$$

For the Tait equation (eq 2)

$$\rho = \rho_0 \Big/ \left[1 - C_T \ln\left(\frac{B_T + P}{B_T + P_0}\right)\right] \tag{2}$$

the following temperature dependence is used for the parameter B_T:

$$B_T = b_0 + b_1\frac{T}{E_T} + b_2\left(\frac{T}{E_T}\right)^2 + b_3\left(\frac{T}{E_T}\right)^3$$

The parameter C_T is a temperature independent constant.

Along with a deviation plot, other statistical values are desirable to evaluate the correlation. The absolute (RMSD) and relative (RMSDr) root-mean-square deviations and the mean deviation (bias) are used as statistical values for the TRIDEN fits.

$$\text{RMSD} = \sqrt{\frac{1}{n}\sum_n(\rho_{exp} - \rho_{calc})^2} \tag{3}$$

$$\text{RMSDr} = 100\sqrt{\frac{1}{n}\sum_n\left(\frac{\rho_{exp} - \rho_{calc}}{\rho_{exp}}\right)^2} \tag{4}$$

$$\text{bias} = \frac{1}{n}\sum_n(\rho_{exp} - \rho_{calc}) \tag{5}$$

The TRIDEN parameters for the Tait equation, parameters for the Rackett equation, the temperature and pressure ranges covered, and additional statistical values are given in Table 3. The units are K, MPa, and kg·m^{-3}.

In Figures 4 and 5 the relative deviations between experimental values and the correlation are shown. The deviations are usually within ±0.04% except at some points at the extremes of temperatures.

The deviations between the TRIDEN correlation for γ-butyrolactone and the densities of Fornefeld-Schwarz et al.[12] at 293 K are −0.04% at all pressures (up to 10 MPa). A comparison was also made between the DDB-Pure[11] correlations of experimental saturated liquid densities from different researchers and the TRIDEN correlations. The very good relative root-mean-square deviations of 0.22% for γ-butyrolactone (from 273 K to 473 K) and 0.07% for NMP (from 273 K to 373 K) are a further indication of the good quality of the measurements and the correlation.

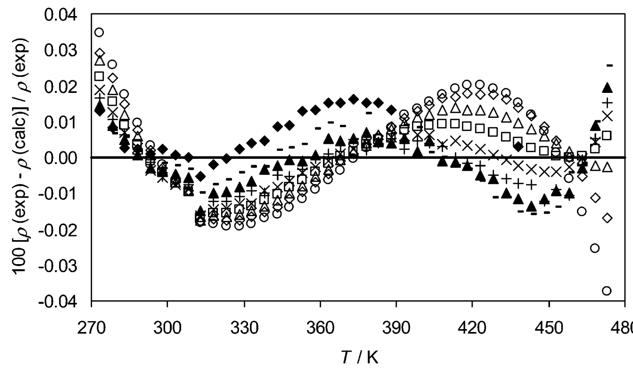

Figure 4. Relative deviations between experimental densities and the TRIDEN correlation for γ-butyrolactone: ○, <5 MPa; ◇, 5 MPa; △, 10 MPa; □, 15 MPa; ×, 20 MPa; +, 25 MPa; ▲, 30 MPa; −, 35 MPa; ◆, 40 MPa.

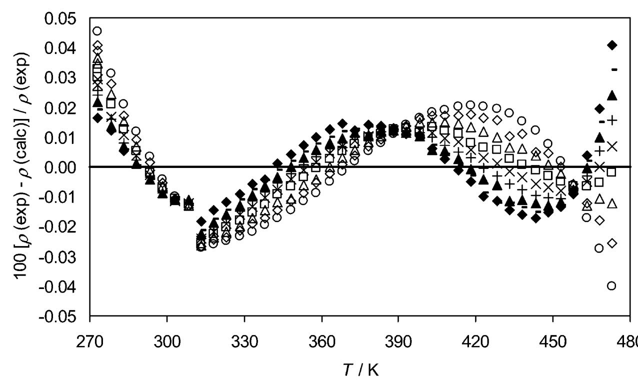

Figure 5. Relative deviations between experimental densities and the TRIDEN correlation for NMP: ○, <5 MPa; ◇, 5 MPa; △, 10 MPa; □, 15 MPa; ×, 20 MPa; +, 25 MPa; ▲, 30 MPa; −, 35 MPa; ◆, 40 MPa.

Summary

Densities in the compressed liquid state were presented for γ-butyrolactone and N-methyl-2-pyrrolidone (NMP) for temperatures between 273 K and 473 K and pressures up to 40 MPa. These measurements represent a wide extension of the $P\rho T$ data for γ-butyrolactone and NMP. All data were correlated with the TRIDEN model and show very good agreement with other published densities.

Table 3. Parameters for the TRIDEN Correlation Model for γ-Butyrolactone and NMP: Temperature Range, Pressure Range, Number of Data Points, Tait Parameters, and Rackett Parameters, and Absolute (RMSD) and Relative (RMSDr) Root-Mean-Square Deviations and the Mean Deviation (bias) as Statistical Values for the TRIDEN Fit

	γ-butyrolactone	NMP
T_{min}/K	273.2	273.2
T_{max}/K	473.1	473.1
P_{min}/MPa	0.26	0.26
P_{max}/MPa	40	40
ρ_{min}/kg·m^{-3}	946.8	865.2
ρ_{max}/kg·m^{-3}	1167.7	1067.7
no. of data points	353	370
c_0	0.101 086	0.089 074
b_0/MPa	446.139	322.577
b_1/MPa	−34.4609	10.1783
b_2/MPa	−27.5124	−33.1819
b_3/MPa	3.810 49	4.033 94
E_T/K	100	100
A_R/kg·m^{-3}	27.7137	29.4842
B_R	0.140 804	0.1520 53
C_R/K	851.568	837.678
D_R	0.273 244	0.277 313
RMSD/kg·m^{-3}	0.1120	0.1377
RMSDr/%	0.0105	0.0139
bias/kg·m^{-3}	−0.000 76	0.001 59

The density measurements for γ-butyrolactone and NMP are a continuation of the density measurements performed for toluene, carbon dioxide, carbonyl sulfide, hydrogen sulfide, sulfur hexafluoride, dinitrogen monoxide, R227ea, sulfur dioxide, some ethers (MTPE, ETBE, and DIPE), and mixtures (DIPE/1-butanol).[1−7]

Literature Cited

(1) Ihmels, E. C.; Gmehling, J. Densities of Toluene, Carbon Dioxide, Carbonyl Sulfide, and Hydrogen Sulfide over a Wide Temperature and Pressure Range in the Sub- and Supercritical State. *Ind. Eng. Chem. Res.* **2001**, *40*, 4470−4477.

(2) Ihmels, E. C.; Gmehling, J. Densities of Sulfur Hexafluoride and Dinitrogen Monoxide over a Wide Temperature and Pressure Range in the Sub- and Supercritical State. *Int. J. Thermophys.* **2002**, *23*, 709−743.

(3) Ihmels, E. C. Experimentelle Bestimmung, Korrelation und Vorhersage von Dichten und Dampfdrücken. Thesis, University of Oldenburg, Shaker Verlag: Aachen, 2002; www.shaker.de.

(4) Ihmels, E. C.; Horstmann, S.; Fischer, K.; Scalabrin, G.; Gmehling, J. Compressed Liquid and Supercritical Densities of 1,1,1,2,3,3,3-Heptafluoropropane (R227ea). *Int. J. Thermophys.* **2002**, *23*, 1571−1585.

(5) Ihmels, E. C.; Gmehling, J. Compressed Liquid Densities of Methyl *tert*-Butyl Ether (MTBE), Ethyl *tert*-Butyl Ether (ETBE), and Diisopropyl Ether (DIPE). *J. Chem. Eng. Data* **2002**, *47*, 1307−1313.

(6) Ihmels, E. C.; Gmehling, J. Liquid Densities and Excess Volumes of Diisopropyl Ether (DIPE) + 1-Butanol Mixtures from 273 to 473 K and Pressures up to 35 MPa. *J. Chem. Eng. Data* **2002**, *47*, 1314−1319.

(7) Ihmels, E. C.; Lemmon E. W.; Gmehling, J. A Helmholtz-type Equation of State and Compressed Liquid and Supercritical Densities for Sulfur Dioxide. *Fluid Phase Equilib.*, submitted

(8) Wagner, W.; Pruss, A. The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use. *J. Phys. Chem. Ref. Data* **2002**, *31* (2), 387−535.

(9) Watanabe, K.; Dooley, R. B. *The International Association for the Properties of Water and Steam, Release on the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use*; Fredericia: Denmark, 1996; www.iawps.org.

(10) Younglove, B. A.; Ely, J. F. Thermophysical Properties of Fluids. II. Methane, Ethane, Propane, Isobutane, and Normal Butane. *J. Phys. Chem. Ref. Data* **1987**, *16*, 577−798.

(11) *Dortmund Data Bank for Pure Component Properties (DDB-Pure)*; DDBST GmbH: Oldenburg, Germany, 2002; www.ddbst.de.

(12) Fornefeld-Schwarz, U.; Klein, A.; Svejda, P. Densities and Isothermal Compressibilities of Liquid Mixtures of γ-Butyrolactone, γ-Valerolactone, δ-Valerolactone, or ϵ-Caprolactone + Benzene, Toluene, or Ethylbenzene at 293.15 K and Pressures up to 10 MPa. *ELDATA: Int. Electron. J. Phys.-Chem. Data* **1997**, *3*, 131−148.

Received for review July 17, 2002. Accepted August 28, 2002. The authors would like to thank the "Max Buchner-Forschungsstiftung" for the financial support of this work.

JE0255877