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$P\rho T$ Behavior of Several Chemicals from Biomass

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Supporting Information

ABSTRACT: Densities of levulinic acid, ethyl levulinate, butyl levulinate, furfural, and furfuryl alcohol have been measured using a high-pressure, high-temperature vibrating tube densimeter system over a temperature range from 283.15 to 338.15 K and a pressure range from 0.1 to 60.0 MPa. In the case of levulinic acid, the temperature range was from 308.15 to 338.15 K. The experimental densities have been satisfactorily correlated with the temperature and pressure using the TRIDEN equation. Finally, from the measured densities, some thermodynamic properties, isobaric thermal expansion and isothermal compressibility, have been calculated.

INTRODUCTION

One of the most important targets of green chemistry is the use of renewable raw materials, that is, the production of chemicals from biomass rather than fossil resources, such as oil, natural gas, or coal. The main problems of using these fossil resources are that they are not renewable and their availability is diminishing rapidly. Solvents from sustainable sources, including those from biomass, which are usually obtained by fermentation, enzymatic, or esterification processes, can be used for a number of industrial processes. For instance, ethyl lactate from biorefineries is now used in the paint industry, in some processes replacing solvents such as *N*-methylpyrrolidone, xylene, toluene, acetone, and various halogenated chemicals.[1] However, the use of these raw materials from biomass is restricted because of the limited knowledge of their molecular and thermophysical properties. This information will luckily lead to scientists using them in new chemical processes, such as synthesis routes, analysis methods, or purification processes, to substitute traditional materials that have been proven to have poor environmental features. Furthermore, the mentioned information could be used for possible industrial applications in the implementation of the studies carried out. However, a review of the literature has revealed that there are not so many of these new green solvents from biomass completely characterized; therefore, their application is limited to the scarce knowledge there is about them.

For these reasons, we have initiated the study of several families of chemicals from biomass in terms of physicochemical properties. The present work is the continuation of a series of papers in which we have obtained several molecular information from thermophysical properties.[2] In this case, we present the pressure−density−temperature ($P\rho T$) behavior of several chemicals that can be classified as green. This study provides an important part of the thermodynamic information for the studied compounds, and the experimental values of density and derived coefficients are supposed to be required for many industrial purposes, including process design.

The selected solvents are included in the furfural family, 2-furaldehyde (CAS number 98-01-1) and 2-(hydroximethyl)-furan (furfuryl alcohol, CAS number 98-00-0), and levulinic acid family, 4-oxopentanoic acid (levulinic acid, CAS number 123-76-2), ethyl 4-oxopentanoate (ethyl levulinate, CAS number 539-88-8), and butyl 4-oxopentanoate (butyl levulinate, CAS number 2052-15-5). The use of carbohydrates as the basis on the production of all of these chemicals makes them renewable products; furfural and related compounds can be obtained from lignocellulose sources through a breaking up procedure of the raw material and a posterior dehydration of the obtained pentoses. Analogously, from dehydration and hydrolysis of cellulose and hexoses, levlulinic acid and related chemicals studied in this work can be obtained.

The $P\rho T$ measurements were carried out over a temperature range from 283.15 to 338.15 K and a pressure range from 0.1 to 60.0 MPa for all of the studied chemicals, except for levulinic acid, in which, the temperature measurement range was from 308.15 to 338.15 K. Experimental density data were fitted to the TRIDEN equation,[3] and from the fitting equation, related properties, such as isobaric thermal expansion, α, and isothermal compressibility, κ_T, have been obtained.

EXPERIMENTAL SECTION

The solvents derived from biomass used in this study were provided by Sigma-Aldrich; furfural, furfuryl alcohol, and ethyl levulinate had a purity of 99%, while the purity of levulinic acid and ethyl levulinate was 98%. All of the compounds were used without further purification because the impurities are in such a low concentration that the physical properties are almost unaffected within the quoted uncertainty of the measurements.[4]

Densities were measured using a high-pressure, high-temperature Anton Paar DMA HP cell connected to an evaluation unit Anton Paar DMA 5000. The density of the sample was determined by measuring the oscillation period of the U-shaped tube made from Hastelloy C-276 gold. The cell temperature is controlled by means of an integrated Peltier thermostat with an uncertainty of $\pm 1 \times 10^{-3}$ K. The required pressure was created by a hand pump 750.1100 from Sitec, Switzerland, and

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Table 1. Experimental Densities as a Function of the Temperature and Pressure

	ρ (kg m^{-3}) at P (MPa)									
T (K)	0.1	2.5	5.0	7.5	10.0	20.0	30.0	40.0	50.0	60.0
					Levulinic Acid					
308.15	1127.38	1128.99	1130.42	1131.77	1133.18	1138.69	1143.68	1148.53	1153.10	1157.49
313.15	1123.08	1124.62	1126.05	1127.53	1128.82	1134.37	1139.49	1144.41	1149.11	1153.55
318.15	1118.79	1120.51	1121.94	1123.36	1124.81	1130.52	1135.67	1140.63	1145.41	1149.86
323.15	1114.50	1116.04	1117.59	1119.09	1120.48	1126.13	1131.44	1136.52	1141.40	1146.07
328.15	1110.21	1111.85	1113.40	1114.92	1116.46	1122.16	1127.62	1132.76	1137.68	1142.31
333.15	1105.93	1107.55	1109.12	1110.65	1112.15	1117.98	1123.46	1128.77	1133.84	1138.61
338.15	1101.65	1103.31	1104.91	1106.41	1108.00	1113.99	1119.61	1125.03	1130.02	1134.93
					Ethyl Levulinate					
283.15	1022.17	1023.78	1025.35	1026.80	1028.39	1034.30	1039.92	1045.26	1050.26	1055.02
288.15	1017.28	1018.83	1020.50	1022.13	1023.69	1029.78	1035.50	1040.89	1045.98	1050.87
293.15	1012.39	1013.99	1015.71	1017.33	1018.97	1025.19	1031.00	1036.59	1041.81	1046.78
298.15	1007.49	1009.16	1010.86	1012.55	1014.22	1020.54	1026.58	1032.19	1037.51	1042.62
303.15	1002.60	1004.38	1006.14	1007.84	1009.53	1016.04	1022.16	1027.97	1033.39	1038.57
308.15	997.71	999.50	1001.30	1003.03	1004.77	1011.45	1017.72	1023.63	1029.14	1034.38
313.15	992.81	994.61	996.45	998.34	1000.11	1006.88	1013.30	1019.36	1025.03	1030.38
318.15	987.91	989.78	991.59	993.52	995.31	1002.33	1008.90	1015.00	1020.73	1026.25
323.15	983.00	984.92	986.83	988.74	990.60	997.80	1004.52	1010.80	1016.70	1022.29
328.15	978.08	980.07	982.04	983.98	985.93	993.32	1000.16	1006.57	1012.61	1018.21
333.15	973.16	975.21	977.18	979.26	981.23	988.70	995.68	1002.30	1008.42	1014.20
338.15	968.23	970.33	972.37	974.48	976.52	984.27	991.33	998.07	1004.25	1010.18
					Butyl Levulinate					
283.15	983.32	984.86	986.45	988.02	989.51	995.45	1001.00	1006.25	1011.28	1016.00
288.15	978.84	980.40	982.01	983.61	985.18	991.20	996.85	1002.28	1007.37	1012.24
293.15	974.36	975.97	977.58	979.26	980.88	987.06	992.85	998.32	1003.48	1008.45
298.15	969.88	971.50	973.19	974.88	976.52	982.80	988.71	994.26	999.58	1004.68
303.15	965.40	967.11	968.86	970.56	972.25	978.75	984.76	990.51	995.83	1000.95
308.15	960.92	962.60	964.38	966.16	967.88	974.44	980.62	986.44	991.94	997.20
313.15	956.44	958.21	960.08	961.85	963.64	970.37	976.71	982.66	988.21	993.51
318.15	951.95	953.77	955.55	957.43	959.25	966.21	972.57	978.69	984.40	989.77
323.15	947.47	949.27	951.24	953.10	955.00	962.03	968.65	974.79	980.64	986.12
328.15	942.98	944.81	946.79	948.73	950.63	957.85	964.58	970.80	976.74	982.41
333.15	938.49	940.36	942.48	944.45	946.43	953.79	960.65	967.07	973.14	978.71
338.15	933.98	935.82	937.91	940.00	941.97	949.56	956.65	963.17	969.21	975.04
					Furfuryl Alcohol					
283.15	1144.15	1145.55	1146.88	1148.24	1149.54	1154.60	1159.52	1164.11	1168.39	1172.61
288.15	1139.55	1140.95	1142.38	1143.70	1145.07	1150.25	1155.17	1159.88	1164.36	1168.60
293.15	1134.92	1136.37	1137.75	1139.17	1140.53	1145.76	1150.81	1155.64	1160.18	1164.50
298.15	1130.28	1131.78	1133.21	1134.58	1136.01	1141.46	1146.55	1151.48	1156.06	1160.47
303.15	1125.62	1127.16	1128.60	1130.04	1131.46	1136.99	1142.21	1147.13	1151.87	1156.38
308.15	1120.94	1122.47	1123.97	1125.47	1126.95	1132.59	1137.96	1142.97	1147.80	1152.36
313.15	1116.24	1117.74	1119.37	1120.82	1122.31	1128.09	1133.47	1138.66	1143.59	1148.24
318.15	1111.51	1113.14	1114.74	1116.24	1117.79	1123.65	1129.19	1134.49	1139.44	1144.25
323.15	1106.75	1108.29	1109.98	1111.53	1113.09	1119.09	1124.74	1130.09	1135.15	1140.06
328.15	1101.97	1103.58	1105.26	1106.84	1108.45	1114.58	1120.39	1125.88	1131.10	1136.03
333.15	1097.14	1098.79	1100.45	1102.16	1103.76	1110.07	1115.93	1121.54	1126.85	1131.86
338.15	1092.29	1093.99	1095.70	1097.45	1099.11	1105.52	1111.60	1117.27	1122.68	1127.73
					2-Furaldehyde					
283.15	1171.20	1172.75	1174.23	1175.67	1177.08	1182.64	1187.94	1193.01	1197.75	1202.36
288.15	1165.89	1167.49	1168.96	1170.48	1171.96	1177.63	1183.06	1188.09	1193.03	1197.73

Table 1. Continued

	ρ (kg m^{-3}) at P (MPa)									
T (K)	0.1	2.5	5.0	7.5	10.0	20.0	30.0	40.0	50.0	60.0
293.15	1160.58	1162.20	1163.77	1165.27	1166.76	1172.58	1178.13	1183.41	1188.40	1193.22
298.15	1155.25	1156.93	1158.48	1160.07	1161.63	1167.58	1173.21	1178.56	1183.64	1188.52
303.15	1149.92	1151.65	1153.26	1154.87	1156.47	1162.54	1168.39	1173.80	1179.00	1183.95
308.15	1144.59	1146.33	1148.01	1149.68	1151.26	1157.51	1163.38	1168.98	1174.26	1179.38
313.15	1139.23	1141.04	1142.78	1144.41	1146.09	1152.50	1158.51	1164.27	1169.69	1174.88
318.15	1133.87	1135.69	1137.42	1139.17	1140.84	1147.39	1153.56	1159.38	1164.96	1170.23
323.15	1128.50	1130.38	1132.08	1133.90	1135.70	1142.34	1148.71	1154.68	1160.35	1165.70
328.15	1123.11	1125.00	1126.85	1128.70	1130.45	1137.30	1143.75	1149.89	1155.58	1161.12
333.15	1117.70	1119.63	1121.52	1123.42	1125.15	1132.27	1138.85	1145.13	1151.03	1156.63
338.15	1112.28	1114.28	1116.19	1118.13	1119.97	1127.14	1133.93	1140.32	1146.32	1152.09

Table 2. Comparison between Experimental and Literature Density Data, ρ, at Atmospheric Pressure and T = 293.15 K

	ρ (kg m^{-3})	
compound	experimental	literature
ethyl levulinate	1012.39	1013.36,[1] 1013.46[2]
butyl levulinate	974.36	974.52,[1] 973.50[2]
furfuryl alcohol	1134.92	1135.1[3]
2-furaldehyde	1160.58	1159.8[3]

measured by a pressure transducer US181 from Measuring Specialties, Hampton, VA. The uncertainty in the pressure measurement is 5 kPa. To evacuate the whole apparatus, a vacuum pump was employed.

The sample density, ρ, is related to the oscillation period, τ, by the following equation:

$$\rho = \sum_{i,j,k} a_{ijk} \tau^i T^j P^k \quad (1)$$

The parameters a_{ijk} can be evaluated using several fluids of known density;[5−7] we have employed hexane, water, and dichloromethane to cover a wide range of densities. This calibration was checked by measuring the densities of toluene over a wide range of temperatures and pressures, with the agreement between measured and reference densities[8] being satisfactory. The estimated uncertainty of our density measurements is 1×10^{-2} kg m^{-3}

RESULTS AND DISCUSSION

The experimental density data are reported in Table 1; in the case of levulinic acid, the density measurements were started from T = 308.15 K because of its high melting point ($T_m \approx 310.15$ K).[9]

Literature density data for the studied compounds is very scarce, and the few reported values have been measured only at atmospheric pressure. On one hand, we report in Table 2 the comparison between experimental and literature density data[10−12] at atmospheric pressure and T = 293.15 K. On the other hand, we show in Figure 1 the comparison also at atmospheric pressure but at different temperatures between our measured densities and previously reported data.[13−15]

The measured densities have been correlated with temperature and pressure using the three-dimensional PρT correlating model TRIDEN. In this model, the Tait equation[16] for isothermal compressed densities was combined with a modified Rackett equation[17] for the liquid saturation densities.

$$\rho_0 = \frac{A_R}{B_R^{[1+(1-T/C_R)^{D_R}]}} \quad (2)$$

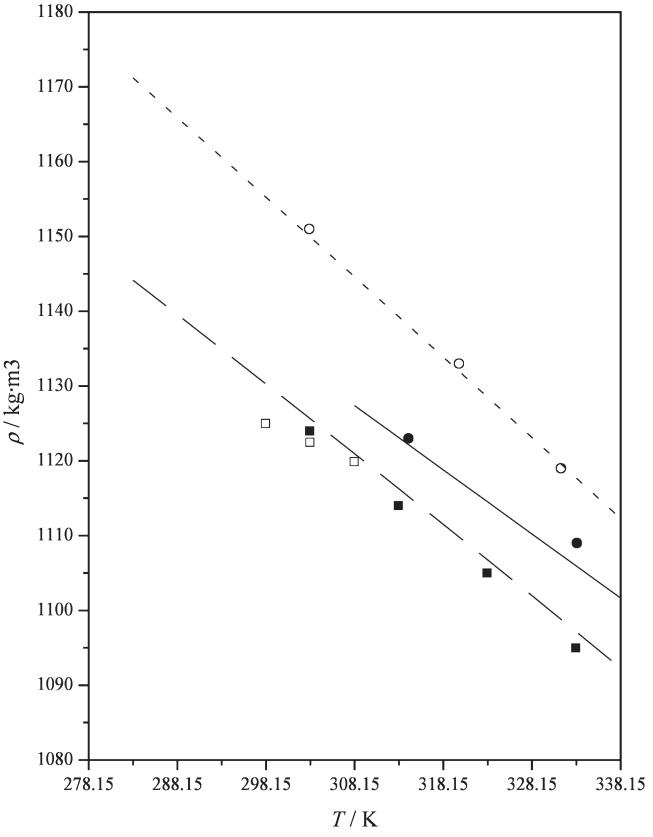

Figure 1. Comparison at atmospheric pressure and different temperatures between our experimental data and previously reported ones: (—) levulinic acid, (- - -) furfuryl alcohol, (· · ·) 2-furaldehyde, (●) ref 13, (□) ref 14, (■) ref 15, and (○) ref 13.

$$\rho = \frac{\rho_0}{1 - C_T \ln\left(\frac{B_T + P}{B_T + P_0}\right)} \quad (3)$$

$$B_T = b_0 + b_1\left(\frac{T}{E_T}\right) + b_2\left(\frac{T}{E_T}\right)^2 + b_3\left(\frac{T}{E_T}\right)^3 \quad (4)$$

The reference pressure is set to P_0 = 0.1 MPa and the corresponding reference densities, ρ_0, were correlated with eq 2. The parameter C_T in eq 4 was treated as temperature-independent.

Table 3. Parameters of the TRIDEN Equation Together with the Corresponding Relative Root-Mean-Square Deviations, RMSDr

	levulinic acid	ethyl levulinate	butyl levulinate	furfuryl alcohol	2-furaldehyde
A_R (kg m^{-3})	442.44	575.14	285.28	723.91	296.32
B_R	0.5613	0.662346	0.471164	0.719769	0.450031
C_R (K)	679.83856	430.36441	655.97326	412.92686	637.09213
D_R	0.79267	0.863809	0.652184	0.808908	0.555875
C_T	0.06771	0.08122	0.08394	0.07178	0.07421
b_0 (MPa)	164.11747	349.27936	339.15101	344.10761	385.49943
b_1 (MPa)	67.32171	−32.65437	−30.34597	−26.73177	−33.13604
b_2 (MPa)	−35.57806	−19.32474	−19.57577	−13.31125	−17.0538
b_3 (MPa)	3.52129	2.85241	2.92532	1.62393	2.28943
E_T (K)	94.67748	83.56373	84.57578	77.56758	75.74244
RMSDr (%)	0.00855	0.00370	0.00527	0.00428	0.00518

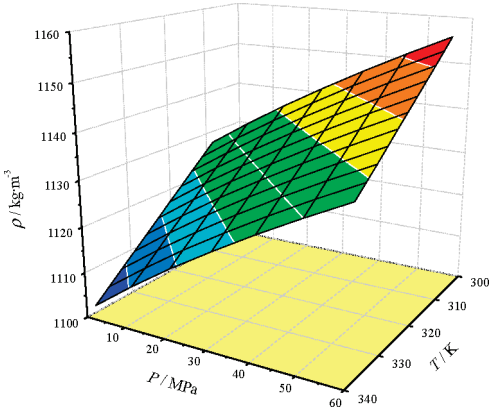

Figure 2. Correlated densities for levulinic acid as function of the temperature and pressure.

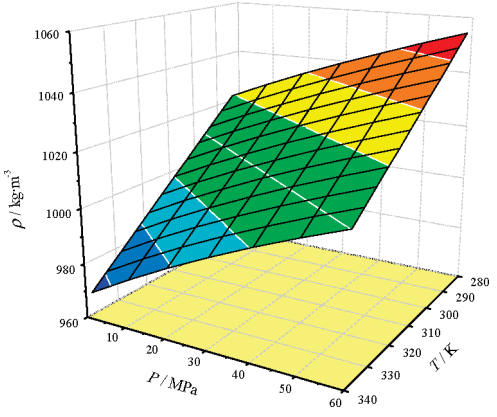

Figure 3. Correlated densities for ethyl levulinate as function of the temperature and pressure.

The relative root-mean-square deviations, RMSDr, were used as statistical values for the TRIDEN fits

$$\mathrm{RMSDr}\ (\%) = 100\left(\frac{1}{n}\sum_{i=1}^{n}\left(\frac{\rho_{i,\mathrm{exp}} - \rho_{i,\mathrm{cal}}}{\rho_{i,\mathrm{exp}}}\right)^2\right)^{1/2} \qquad (5)$$

where n is the number of experimental data.

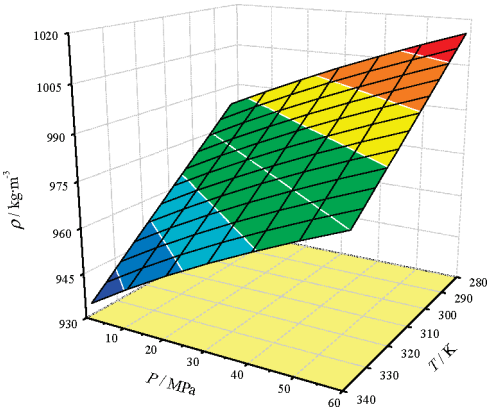

Figure 4. Correlated densities for butyl levulinate as function of the temperature and pressure.

The TRIDEN parameters along with the corresponding deviations were collected in Table 3. RMSDr obtained for the studied chemicals from biomass are quite similar, with the lowest being for ethyl levulinate and the highest being for levulinic acid. Values obtained are of the same order as some others obtained previously for pure fluids.[18,19]

The three-dimensional density plots of the studied liquids calculated from the corresponding TRIDEN equations are shown in Figures 2−6. As expected, density decreases with the temperature for isobars and increases with the pressure for isotherms. Highest values of density are found for 2-furaldehyde, while butyl levulinate shows the lowest values. In previous work,[2] we studied the structure and packing of these chemicals, taking into account not only volumetric properties but also energetic effects. In that work, we pointed out that chemicals from the levulinate family were more compressible, probably because of the esteric impediment in the internal organization of the molecules, while 2-furaldehyde and furfuryl alcohol could be more packed because of a better accommodation of the molecules as a result of the structure formed by the cyclic ether and the small group, alcohol or aldehyde. We can conclude that experimental results obtained in the present work, which extend the range of study in the temperature and pressure, are in excellent agreement with the results obtained previously.

The effects of the temperature and pressure on density are well-described by isobaric thermal expansion, α, and isothermal

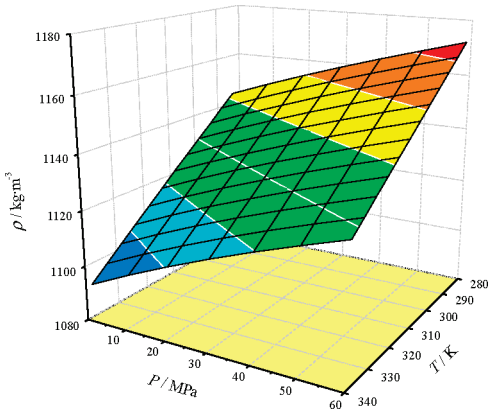

Figure 5. Correlated densities for furfuryl alcohol as function of the temperature and pressure.

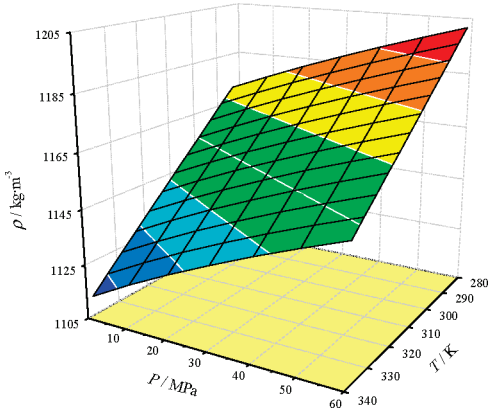

Figure 6. Correlated densities for 2-furaldehyde as function of the temperature and pressure.

compressibility, κ_T, that are defined as

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \quad (6)$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T \quad (7)$$

The temperature and pressure derivatives of density can be evaluated using the TRIDEN equation. The estimated values of isobaric thermal expansion and isothermal compressibility are collected in the Supporting Information.

Both isobaric thermal expansion, α, and isothermal compressibility, κ_T, show the usual behavior of most fluids; values increase with the temperature along isobars and decrease with the pressure along isotherms. Values of isobaric thermal expansion, α, obtained in this work have been compared to those obtained previously at 298.15 K and atmospheric pressure,[2] and results are in good agreement. Higher values for this property have been found for esters ethyl levulinate and butyl levulinate, while levulinic acid shows the lowest values, followed by furfuryl alcohol. In relation to isothermal compressibility, we have found that esters show again higher values, followed by levulinic acid and 2-furaldehyde. Finally, furfuryl alcohol shows the lowest value. Taking into account that it has been pointed out that isothermal compressibility is related to the extent of hydrogen bonds that can be established between molecules of fluids,[20] we can corroborate that levulinic acid and furfuryl alcohol show relatively lower values of these properties.

■ ASSOCIATED CONTENT

Supporting Information. Isobaric thermal expansions, α, as function of the temperature and pressure (Table S1) and isothermal compressibilities, κ_T, as function of the temperature and pressure (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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