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Speed of Sound in Propan-1-ol + Heptane Mixtures under Elevated Pressures

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The speed of sound in propan-1-ol + heptane mixtures was measured over the whole composition range within the temperatures from 293.15 K to 318.15 K and at pressures up to 120 MPa. The effect of pressure and temperature on the speed of sound has been discussed.

1. Introduction

Measurements of the speed of sound at elevated pressures are claimed to be a simple and relatively rapid method of obtaining data which are rather hard to obtain by direct measurements. Ultrasonic speed measurements provided reliable *pVT* data from which the equations of state were derived for some liquids.[1−5] The densities of liquids as functions of pressure derived from ultrasonic speeds are in good agreement with those obtained by direct methods.[6]

The development of high-pressure thermodynamics of mixtures is still unsatisfactory, since most of the research activities have focused hitherto on the high-pressure properties of pure compounds. The present study dealing with the speed of sound in propan-1-ol + heptane mixtures was aimed at the effect of pressure on the speed of sound. This effect provides information important for the calculation of several thermodynamic quantities under elevated pressures (density, heat capacity, and isentropic and isothermal compressibility).

2. Experiment

Chemicals. Propan-1-ol, from Merck, was analytically pure with minimum mass fraction 99.8% of C_3H_7OH; the concentration of water, determined by the Karl Fisher method, was less than 0.02%. Heptane from Merck was of special purity for the analysis with minimum mass fraction 99.5% of C_7H_{16}. The chemicals were degassed in an ultrasonic cleaner and used without further purification. The densities and the speeds of sound in the pure components are compared with literature data in Table 1. The mixtures were prepared by mass. The balance accuracy was $\pm 6 \times 10^{-4}$ g. From the balance accuracy, the uncertainty in the mole fraction of the solutions was estimated to be 3×10^{-6} (in the most unfavorable case).

Ultrasonic Speed Measurements. An apparatus designed and constructed in our laboratory[19] was used for the measurements of the speed of sound in the liquids under test. The measuring set with a single transmitting−receiving ceramic transducer of a frequency of 4 MHz and an acoustic mirror operates on the principle of the pulse−echo-overlap method. The pressure, generated by a hand-operated hydraulic press connected with the pressure vessel by a system of capillary tubes and valves, was measured with a strain gauge system located outside the vessel with an accuracy better than 0.15%. The temperatures were measured with a platinum resistance thermometer (*Ertco Hart 850*) of accuracy ±0.05 K and a resolution of 0.001 K. All temperatures reported in this work are expressed in the International Temperature Scale of 1990 (ITS-90).

Table 1. Comparison of the Speeds of Sound and Densities Obtained in This Work for Pure Components at T = 298.15 K under Atmospheric Pressure with Those Reported in the Literature

component		exp	lit.
heptane	u/m·s^{-1}	1129.92	1129.85,[7] 1130.1,[8] 1130.18,[9] 1136.30[10]
	ρ/kg·m^{-3}	679.68	679.50,[11] 679.57,[12] 679.60,[9] 679.70,[8] 679.81[13]
propan-1-ol	u/m·s^{-1}	1205.82	1205.17,[9] 1205.30,[14] 1206.40[15]
	ρ/kg·m^{-3}	799.62	799.55,[16] 799.58 ,[17] 799.624,[18] 799.69[12]

Redistilled water was used as the standard liquid for determining the ultrasonic path length. The speed of sound in water under atmospheric pressure was calculated from the polynomial of Marczak[20] and for higher pressures from the equation of Kell and Whalley.[2] The uncertainty of the speed of sound measurements was estimated to be 0.03% at atmospheric pressure, 0.04% under pressures up to 60 MPa, and 0.05% for pressures ranging from 60 MPa to 120 MPa. More details of the measuring set, calibration, and measurement procedure can be found in the previous paper.[19]

3. Measurement Results

The ultrasonic speeds for the propan-1-ol + heptane mixtures were measured within the whole concentration range from 293 K to 318 K in about 5 K steps and under the pressures (15, 30, 45, 60, 75, 90, 100, 110, and 120) MPa. The experimental values are listed in Table 2.

The dependencies of the speed of sound on temperature at atmospheric pressure can be approximated satisfactorily by second-order polynomials of the type

$$u_0 = \sum_{j=0}^{2} b_j T^j \qquad (1)$$

where u_0 is the speed of sound at atmospheric pressure p_0 and b_j are the polynomial coefficients calculated by the least-squares method. The coefficients b_j and the mean

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Table 2. Speed of Sound in Propan-1-ol (1) + Heptane (2) Mixtures Measured at Pressures up to 120 MPa within the Temperature Range 293 K to 318 K (x_1 = the Mole Fraction of Propan-1-ol)

x_1	p/MPa	T/K	u/m·s^{-1}	x_1	p/MPa	T/K	u/m·s^{-1}	x_1	p/MPa	T/K	u/m·s^{-1}	x_1	p/MPa	T/K	u/m·s^{-1}
0.0000	0.10	293.15	1151.69	0.1008	45.59	303.21	1379.27	0.3008	101.32	313.16	1576.18	0.6027	30.40	318.23	1261.36
0.0000	0.10	298.16	1129.87	0.1008	45.59	308.22	1363.15	0.3008	101.32	318.18	1563.29	0.6027	45.59	293.10	1414.52
0.0000	0.10	303.06	1108.88	0.1008	45.59	313.13	1347.63	0.3008	111.45	293.14	1663.26	0.6027	45.59	298.19	1398.60
0.0000	0.10	308.08	1087.42	0.1008	45.59	318.19	1331.61	0.3008	111.45	298.14	1650.06	0.6027	45.59	303.15	1383.20
0.0000	0.10	313.10	1066.12	0.1008	60.79	293.19	1479.59	0.3008	111.45	303.25	1636.87	0.6027	45.59	308.14	1368.09
0.0000	0.10	318.18	1044.54	0.1008	60.79	298.18	1464.22	0.3008	111.45	308.14	1624.08	0.6027	45.59	313.13	1353.01
0.0000	15.20	293.20	1256.33	0.1008	60.79	303.20	1448.77	0.3008	111.45	313.15	1611.46	0.6027	45.59	318.16	1338.20
0.0000	15.20	303.17	1218.64	0.1008	60.79	308.21	1433.56	0.3008	111.45	318.17	1598.98	0.6027	60.79	293.14	1478.74
0.0000	15.20	308.08	1200.43	0.1008	60.79	313.12	1419.00	0.3008	121.58	293.17	1695.52	0.6027	60.79	298.23	1463.59
0.0000	15.20	313.10	1182.05	0.1008	60.79	318.17	1403.88	0.3008	121.58	298.15	1682.68	0.6027	60.79	303.08	1449.55
0.0000	15.20	318.18	1163.39	0.1008	75.99	293.13	1541.78	0.3008	121.58	303.16	1669.91	0.6027	60.79	308.18	1435.02
0.0000	30.40	293.18	1341.50	0.1008	75.99	298.17	1526.78	0.3008	121.58	308.10	1657.47	0.6027	60.79	313.14	1420.87
0.0000	30.40	303.13	1306.98	0.1008	75.99	303.21	1512.06	0.3008	121.58	313.15	1645.10	0.6027	60.79	318.15	1406.89
0.0000	30.40	308.07	1290.28	0.1008	75.99	308.20	1497.71	0.3008	121.58	318.17	1633.00	0.6027	75.99	293.15	1537.84
0.0000	30.40	313.12	1273.35	0.1008	75.99	313.14	1483.74	0.4992	0.10	293.12	1158.17	0.6027	75.99	298.22	1523.54
0.0000	30.40	318.17	1256.47	0.1008	75.99	318.15	1469.44	0.4992	0.10	298.13	1136.97	0.6027	75.99	303.15	1509.94
0.0000	45.59	293.19	1416.60	0.1008	91.19	293.10	1598.97	0.4992	0.10	303.16	1116.00	0.6027	75.99	308.17	1496.27
0.0000	45.59	298.18	1400.09	0.1008	91.19	298.17	1584.48	0.4992	0.10	308.20	1095.17	0.6027	75.99	313.12	1482.86
0.0000	45.59	303.07	1384.42	0.1008	91.19	303.21	1570.45	0.4992	0.10	313.15	1074.76	0.6027	75.99	318.27	1469.25
0.0000	45.59	308.07	1368.71	0.1008	91.19	308.22	1556.66	0.4992	0.10	318.13	1054.27	0.6027	91.19	293.14	1592.55
0.0000	45.59	313.12	1352.98	0.1008	91.19	313.16	1543.31	0.4992	30.40	293.17	1340.47	0.6027	91.19	298.19	1578.99
0.0000	45.59	318.17	1337.39	0.1008	101.32	293.14	1634.71	0.4992	30.40	298.15	1323.25	0.6027	91.19	303.14	1565.91
0.0000	60.79	293.20	1484.48	0.1008	101.32	298.16	1620.64	0.4992	30.40	303.14	1306.45	0.6027	91.19	308.18	1552.76
0.0000	60.79	298.19	1468.69	0.1008	101.32	303.17	1607.10	0.4992	30.40	308.20	1289.63	0.6027	91.19	313.12	1540.04
0.0000	60.79	303.18	1453.68	0.1008	101.32	308.20	1593.69	0.4992	30.40	313.09	1273.27	0.6027	91.19	318.21	1527.20
0.0000	60.79	308.12	1438.95	0.1008	101.32	313.19	1580.60	0.4992	30.40	318.14	1256.94	0.6027	101.32	293.18	1626.90
0.0000	60.79	313.12	1424.30	0.1008	101.32	318.17	1567.68	0.4992	45.59	293.13	1412.63	0.6027	101.32	298.15	1613.86
0.0000	60.79	318.17	1409.63	0.1008	111.45	293.15	1668.88	0.4992	45.59	298.16	1396.69	0.6027	101.32	303.08	1601.16
0.0000	75.99	293.20	1546.46	0.1008	111.45	298.18	1655.13	0.4992	45.59	303.16	1380.91	0.6027	101.32	308.24	1588.13
0.0000	75.99	298.11	1531.64	0.1008	111.45	303.18	1641.96	0.4992	45.59	308.20	1365.20	0.6027	101.32	313.12	1575.87
0.0000	75.99	303.17	1517.17	0.1008	111.45	308.22	1628.88	0.4992	45.59	313.15	1349.89	0.6027	101.32	318.20	1563.49
0.0000	75.99	308.12	1503.23	0.1008	111.45	313.19	1616.26	0.4992	45.59	318.13	1334.78	0.6027	111.45	293.16	1659.80
0.0000	75.99	313.10	1489.21	0.1008	111.45	318.17	1603.70	0.4992	60.79	293.16	1478.01	0.6027	111.45	298.13	1647.11
0.0000	75.99	318.09	1475.54	0.1008	121.58	293.13	1701.59	0.4992	60.79	298.15	1462.72	0.6027	111.45	303.10	1634.70
0.0000	91.19	293.20	1603.69	0.1008	121.58	298.14	1688.80	0.4992	60.79	303.15	1447.96	0.6027	111.45	308.16	1622.27
0.0000	91.19	298.15	1589.43	0.1008	121.58	303.19	1675.42	0.4992	60.79	308.19	1432.98	0.6027	111.45	313.17	1610.05
0.0000	91.19	303.18	1575.68	0.1008	121.58	308.23	1662.31	0.4992	60.79	313.09	1418.69	0.6027	111.45	318.23	1598.03
0.0000	91.19	308.11	1562.39	0.1008	121.58	313.19	1649.67	0.4992	60.79	318.12	1404.41	0.6027	121.58	293.18	1691.22
0.0000	91.19	313.13	1549.03	0.1008	121.58	318.17	1636.99	0.4992	75.99	293.16	1537.79	0.6027	121.58	298.06	1678.99
0.0000	91.19	318.15	1535.72	0.3008	0.10	293.21	1149.88	0.4992	75.99	298.15	1523.30	0.6027	121.58	303.18	1666.63
0.0000	101.32	293.20	1639.70	0.3008	0.10	298.18	1128.58	0.4992	75.99	303.14	1509.25	0.6027	121.58	308.18	1654.69
0.0000	101.32	298.16	1625.72	0.3008	0.10	303.20	1107.11	0.4992	75.99	308.18	1495.20	0.6027	121.58	313.17	1642.86
0.0000	101.32	303.10	1612.63	0.3008	0.10	308.12	1086.26	0.4992	75.99	313.15	1481.40	0.6027	121.58	318.18	1631.28
0.0000	101.32	308.24	1599.12	0.3008	0.10	313.17	1065.01	0.4992	75.99	318.18	1467.82	0.7016	0.10	293.14	1173.77
0.0000	101.32	313.21	1586.17	0.3008	0.10	318.21	1043.76	0.4992	91.19	293.19	1592.62	0.7016	0.10	298.20	1153.98
0.0000	101.32	318.18	1573.59	0.3008	30.40	293.21	1336.48	0.4992	91.19	298.14	1579.27	0.7016	0.10	303.14	1134.54
0.0000	111.45	293.10	1674.29	0.3008	30.40	298.17	1319.27	0.4992	91.19	303.13	1565.77	0.7016	0.10	308.21	1114.65
0.0000	111.45	298.16	1660.43	0.3008	30.40	303.20	1301.75	0.4992	91.19	308.18	1552.34	0.7016	0.10	313.24	1095.20
0.0000	111.45	298.13	1660.46	0.3008	30.40	308.19	1284.81	0.4992	91.19	313.15	1539.28	0.7016	0.10	318.14	1076.19
0.0000	111.45	303.15	1647.60	0.3008	30.40	313.17	1268.13	0.4992	91.19	318.17	1526.33	0.7016	30.40	293.16	1348.55
0.0000	111.45	308.21	1634.64	0.3008	30.40	318.19	1251.44	0.4992	101.32	293.21	1627.32	0.7016	30.40	298.20	1332.13
0.0000	111.45	313.20	1622.05	0.3008	45.59	293.22	1410.18	0.4992	101.32	298.13	1614.37	0.7016	30.40	303.13	1316.24
0.0000	111.45	318.18	1609.77	0.3008	45.59	298.17	1394.10	0.4992	101.32	303.12	1601.34	0.7016	30.40	308.22	1300.01
0.0000	121.58	293.16	1707.09	0.3008	45.59	303.23	1377.74	0.4992	101.32	308.15	1588.31	0.7016	30.40	313.23	1284.35
0.0000	121.58	298.14	1692.38	0.3008	45.59	308.16	1361.97	0.4992	101.32	313.15	1575.54	0.7016	30.40	318.15	1268.94
0.0000	121.58	303.10	1681.25	0.3008	45.59	313.12	1346.51	0.4992	101.32	318.16	1563.05	0.7016	45.59	293.17	1418.34
0.0000	121.58	308.17	1668.58	0.3008	45.59	318.19	1330.84	0.4992	111.45	293.21	1660.48	0.7016	45.59	298.19	1403.04
0.0000	121.58	313.13	1656.40	0.3008	60.79	293.19	1476.81	0.4992	111.45	298.15	1647.86	0.7016	45.59	303.12	1388.19
0.0000	121.58	318.17	1644.27	0.3008	60.79	298.17	1461.53	0.4992	111.45	303.11	1635.32	0.7016	45.59	308.20	1373.07
0.1008	0.10	293.22	1147.28	0.3008	60.79	303.21	1446.05	0.4992	111.45	308.11	1622.61	0.7016	45.59	313.22	1358.44
0.1008	0.10	298.15	1125.74	0.3008	60.79	308.15	1431.22	0.4992	111.45	313.17	1610.14	0.7016	45.59	318.15	1344.09
0.1008	0.10	303.22	1103.78	0.3008	60.79	313.15	1416.44	0.4992	111.45	318.15	1598.02	0.7016	60.79	293.18	1481.64
0.1008	0.10	308.22	1082.18	0.3008	60.79	318.19	1401.86	0.4992	121.58	293.23	1692.22	0.7016	60.79	298.18	1467.23
0.1008	0.10	313.15	1061.04	0.3008	75.99	293.20	1537.70	0.4992	121.58	298.14	1679.93	0.7016	60.79	303.14	1453.14
0.1008	0.10	318.18	1039.67	0.3008	75.99	298.17	1523.18	0.4992	121.58	303.11	1667.65	0.7016	60.79	308.21	1438.85
0.1008	15.20	293.22	1251.98	0.3008	75.99	303.21	1508.45	0.4992	121.58	308.10	1655.43	0.7016	60.79	313.23	1425.10
0.1008	15.20	298.17	1232.86	0.3008	75.99	308.17	1494.32	0.4992	121.58	313.16	1643.29	0.7016	60.79	318.15	1411.60
0.1008	15.20	303.16	1213.62	0.3008	75.99	313.17	1480.32	0.4992	121.58	318.13	1631.55	0.7016	75.99	293.20	1539.77
0.1008	15.20	308.12	1194.89	0.3008	75.99	318.18	1466.53	0.6027	0.10	293.13	1164.90	0.7016	75.99	298.18	1526.04
0.1008	15.20	313.14	1176.11	0.3008	91.19	293.10	1594.32	0.6027	0.10	298.18	1144.27	0.7016	75.99	303.13	1512.67
0.1008	15.20	318.18	1157.75	0.3008	91.19	298.19	1580.10	0.6027	0.10	303.15	1123.99	0.7016	75.99	308.23	1499.11
0.1008	30.40	293.22	1336.96	0.3008	91.19	303.21	1566.12	0.6027	0.10	308.21	1103.48	0.7016	75.99	313.15	1486.29
0.1008	30.40	298.17	1319.51	0.3008	91.19	308.14	1552.63	0.6027	0.10	313.10	1083.89	0.7016	75.99	318.17	1473.20
0.1008	30.40	303.21	1301.88	0.3008	91.19	313.15	1539.31	0.6027	0.10	318.20	1063.45	0.7016	91.19	293.20	1593.66
0.1008	30.40	308.22	1284.58	0.3008	91.19	318.17	1526.08	0.6027	30.40	293.13	1343.28	0.7016	91.19	298.17	1580.65
0.1008	30.40	313.15	1267.88	0.3008	101.32	293.16	1629.45	0.6027	30.40	298.19	1326.38	0.7016	91.19	303.13	1567.84
0.1008	30.40	318.20	1250.71	0.3008	101.32	298.10	1616.01	0.6027	30.40	303.14	1309.96	0.7016	91.19	308.12	1555.15
0.1008	45.59	293.11	1411.95	0.3008	101.32	303.17	1602.36	0.6027	30.40	308.11	1293.74	0.7016	91.19	313.11	1542.71
0.1008	45.59	298.16	1395.71	0.3008	101.32	308.16	1589.14	0.6027	30.40	313.12	1277.58	0.7016	91.19	318.16	1530.16

Table 2. (Continued)

x_1	p/MPa	T/K	u/m·s^{-1}	x_1	p/MPa	T/K	u/m·s^{-1}	x_1	p/MPa	T/K	u/m·s^{-1}	x_1	p/MPa	T/K	u/m·s^{-1}
0.7016	101.32	293.19	1627.50	0.7986	45.59	308.15	1379.82	0.7986	121.58	293.11	1691.79	1.0000	60.79	313.17	1451.85
0.7016	101.32	298.18	1614.88	0.7986	45.59	313.11	1365.68	0.7986	121.58	298.20	1679.91	1.0000	60.79	318.12	1439.64
0.7016	101.32	303.13	1602.48	0.7986	45.59	318.12	1351.38	0.7986	121.58	303.11	1668.62	1.0000	75.99	293.20	1557.22
0.7016	101.32	308.16	1589.96	0.7986	60.79	293.13	1486.08	0.7986	121.58	308.09	1657.25	1.0000	75.99	298.14	1544.87
0.7016	101.32	313.13	1578.01	0.7986	60.79	298.17	1471.77	0.7986	121.58	313.10	1645.91	1.0000	75.99	303.15	1532.53
0.7016	101.32	318.16	1565.92	0.7986	60.79	303.13	1458.07	0.7986	121.58	318.14	1634.79	1.0000	75.99	308.12	1520.40
0.7016	111.45	293.18	1659.94	0.7986	60.79	308.14	1444.40	1.0000	0.10	293.19	1222.98	1.0000	75.99	313.16	1508.49
0.7016	111.45	298.17	1647.59	0.7986	60.79	313.10	1431.00	1.0000	0.10	298.12	1205.93	1.0000	75.99	318.12	1496.85
0.7016	111.45	303.13	1635.61	0.7986	60.79	318.15	1417.48	1.0000	0.10	303.12	1188.72	1.0000	91.19	293.20	1607.57
0.7016	111.45	308.17	1623.43	0.7986	75.99	293.12	1543.06	1.0000	0.10	308.20	1171.37	1.0000	91.19	298.14	1595.85
0.7016	111.45	313.20	1611.62	0.7986	75.99	298.17	1529.53	1.0000	0.10	313.17	1154.51	1.0000	91.19	303.17	1584.03
0.7016	111.45	318.17	1600.00	0.7986	75.99	303.10	1516.73	1.0000	0.10	318.20	1137.48	1.0000	91.19	308.20	1572.36
0.7016	121.58	293.16	1690.95	0.7986	75.99	308.19	1503.36	1.0000	15.20	293.12	1308.47	1.0000	91.19	313.15	1561.08
0.7016	121.58	298.18	1678.94	0.7986	75.99	313.08	1490.85	1.0000	15.20	298.11	1292.86	1.0000	91.19	318.12	1549.89
0.7016	121.58	303.12	1667.28	0.7986	75.99	318.14	1477.99	1.0000	15.20	303.14	1277.31	1.0000	101.32	293.18	1639.47
0.7016	121.58	308.09	1655.64	0.7986	91.19	293.16	1595.93	1.0000	15.20	308.20	1263.59	1.0000	101.32	298.14	1628.00
0.7016	121.58	313.22	1643.94	0.7986	91.19	298.26	1583.00	1.0000	15.20	313.16	1248.70	1.0000	101.32	303.17	1616.49
0.7016	121.58	318.09	1632.82	0.7986	91.19	303.10	1570.90	1.0000	30.40	293.22	1379.93	1.0000	101.32	308.19	1605.09
0.7986	0.10	293.14	1185.85	0.7986	91.19	308.20	1558.14	1.0000	30.40	298.15	1365.60	1.0000	101.32	313.15	1594.14
0.7986	0.10	298.17	1166.66	0.7986	91.19	313.11	1546.11	1.0000	30.40	303.24	1350.89	1.0000	101.32	318.11	1583.33
0.7986	0.10	303.12	1147.60	0.7986	91.19	318.16	1533.86	1.0000	30.40	308.13	1336.85	1.0000	111.45	293.17	1669.92
0.7986	0.10	308.15	1128.43	0.7986	101.32	293.17	1629.25	1.0000	30.40	313.16	1322.58	1.0000	111.45	298.14	1658.78
0.7986	0.10	313.08	1109.69	0.7986	101.32	298.25	1616.74	1.0000	30.40	318.16	1308.73	1.0000	111.45	303.19	1647.55
0.7986	0.10	318.08	1090.85	0.7986	101.32	303.09	1604.91	1.0000	45.59	293.21	1444.18	1.0000	111.45	308.16	1636.69
0.7986	30.40	293.12	1355.63	0.7986	101.32	308.14	1592.68	1.0000	45.59	298.14	1430.65	1.0000	111.45	313.22	1625.76
0.7986	30.40	298.15	1339.57	0.7986	101.32	313.11	1580.89	1.0000	45.59	303.13	1417.04	1.0000	111.45	318.17	1615.27
0.7986	30.40	303.12	1324.13	0.7986	101.32	318.11	1569.08	1.0000	45.59	308.13	1403.65	1.0000	121.58	293.16	1699.12
0.7986	30.40	308.13	1308.48	0.7986	111.45	293.14	1661.20	1.0000	45.59	313.16	1390.41	1.0000	121.58	298.14	1688.24
0.7986	30.40	313.16	1293.20	0.7986	111.45	298.13	1649.19	1.0000	45.59	318.14	1377.40	1.0000	121.58	303.18	1677.36
0.7986	30.40	318.13	1277.94	0.7986	111.45	303.12	1637.49	1.0000	60.79	293.21	1502.84	1.0000	121.58	308.11	1666.98
0.7986	45.59	293.12	1424.00	0.7986	111.45	308.11	1625.74	1.0000	60.79	298.14	1490.03	1.0000	121.58	313.17	1656.22
0.7986	45.59	298.16	1408.88	0.7986	111.45	313.12	1614.09	1.0000	60.79	303.20	1477.02	1.0000	121.58	318.17	1645.95
0.7986	45.59	303.12	1394.45	0.7986	111.45	318.13	1602.69	1.0000	60.79	308.13	1464.46				

Table 3. Coefficients of Polynomial Eq 1 for the Speed of Sound within the Temperature Range (293−318) K and Mean Deviations from the Regression Line δu_0

x_1	b_0/m·s^{-1}	b_1/m·s^{-1}·K^{-1}	b_2/m·s^{-1}·K^{-2}	δu_0/m·s^{-1}
0.0000	2681.70	−6.0852	0.002 953	0.08
0.1008	2676.16	−6.0460	0.002 837	0.03
0.3008	2608.17	−5.6462	0.002 294	0.05
0.4992	2642.22	−5.9050	0.002 872	0.08
0.6027	2593.68	−5.6358	0.002 599	0.05
0.7016	2469.37	−4.8929	0.001 615	0.06
0.7986	2449.12	−4.7679	0.001 564	0.07
1.0000	2404.70	−4.5960	0.001 928	0.02

Table 4. Coefficients of Eq 2 and Mean Deviations from the Regression Line δu

	a_{10}	a_{20}	a_{11}	δu
x_1	MPa·s·m^{-1}	MPa·s^2·m^{-2}	MPa·s·m^{-1}·K^{-1}	m·s^{-1}
0.0000	0.393 095 189 9	0.000 158 592 282	−0.000 897 329 094	0.77
0.1008	0.390 504 465 9	0.000 159 343 413	−0.000 888 160 636	0.78
0.3008	0.397 101 404 2	0.000 162 667 167	−0.000 900 470 048	0.69
0.4992	0.405 116 528 4	0.000 167 938 565	−0.000 916 062 060	0.74
0.6027	0.407 693 553 9	0.000 169 574 006	−0.000 910 960 298	0.63
0.7016	0.406 492 479 7	0.000 173 314 515	−0.000 894 221 863	0.65
0.7986	0.415 604 085 7	0.000 177 202 354	−0.000 907 274 183	0.59
1.0000	0.413 361 546 4	0.000 188 478 613	−0.000 848 591 727	0.78

deviations from the regression lines are given in Table 3. The backward stepwise rejection procedure was used to reduce the number of nonzero coefficients.

Since the sensitivity of the pressure gauge is lower than that of both the ultrasonic measuring set and the thermometer, the equation suggested by Sun et al.[21] was chosen in this work for smoothing out the speed of sound, pressure, and temperature values for each solution:

$$p - p_0 = \sum_{i=1}^{m}\sum_{j=0}^{n} a_{ij}(u - u_0)^i T^j \qquad (2)$$

where a_{ij} are the polynomial coefficients calculated by the least-squares method, u is the speed of sound at $p > 0.1$ MPa, and u_0 is the speed calculated from eq 1. The coefficients a_{ij} and the mean deviations from the regression lines are given in Table 4. The stepwise rejection procedure was used to reduce the number of the nonzero coefficients.

To show the effect of temperature and pressure on the additivity of the speeds of sound, the deviations from a mole fraction average, $\Delta u = u - \sum_{i=1}^{2} x_i u_i^\circ$ (where u is the ultrasound speed in the mixture, u_i° are the ultrasound speeds in the pure components, and x_i are the mole fractions of the components), have been calculated.

4. Discussion

The speeds of sound in heptane reported in this work are, within the measurement precision, equal to those reported by Żak et al.[19] However, they are, by about 0.6%, higher than the speeds measured by Muringer et al.[10] It is noteworthy that Muringer's data for the atmospheric pressure seem to be systematically shifted upward by the same value in comparison with the case of speeds in heptane reported in other literature sources (Table 1). For the whole pressure range, the speeds of sound in propan-1-ol at 303.15 K obtained in this experiment differ by less than 1.5% from the data of Hawley et al.,[22] who declared an accuracy of 0.3%, and by 0.3% from the data reported in the *Landolt-Börnstein* tables.[23]

For a given pressure, the speed of sound is decreasing almost linearly with increasing temperature, while, at a given temperature, the speed of sound is increasing nonlinearly with increasing pressure. The speeds of sound as a function of concentration show shallow minima. With increasing pressure the minima move toward higher concentrations of propan-1-ol. Furthermore, for any temperature, the speeds of sound in pure heptane are increasing with increasing pressure more rapidly than those in both the pure propan-1-ol and the binary mixtures (Figure 1). This is probably due to a faster decrease of the

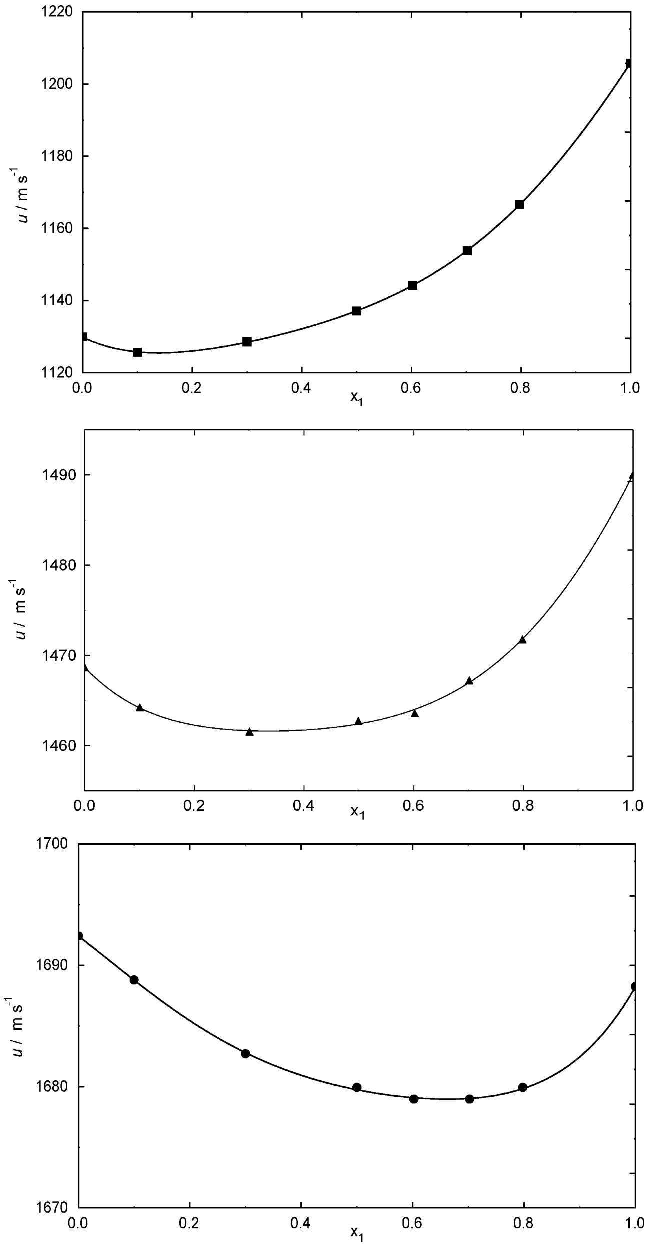

Figure 1. Speed of sound in propan-1-ol + heptane mixtures at 298.15 K: (■) 0.1 MPa; (▲) 60.79 MPa; (●) 121.58 MPa; (—) calculated from the empirical function $u = \sum_{i=0}^{3} a_i x_1^{\,i}$.

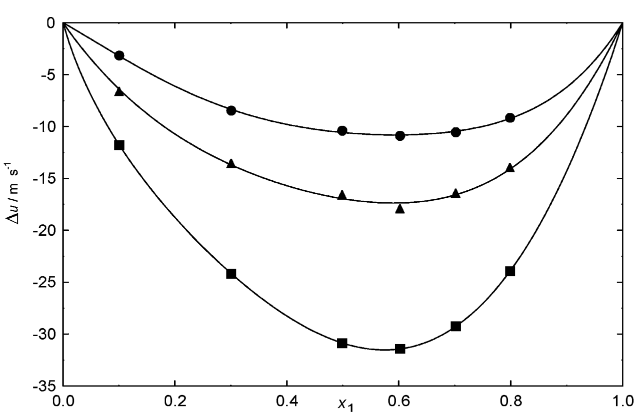

Figure 2. Δu for propan-1-ol + heptane mixtures at 298.15 K: (■) 0.1 MPa; (▲) 60.79 MPa; (●) 121.58 MPa; (—) calculated from the Redlich−Kister equation, $\Delta u = x_1(1 - x_1)\sum_{i=0}^{2} a_i(1 - 2x_1)^i$.

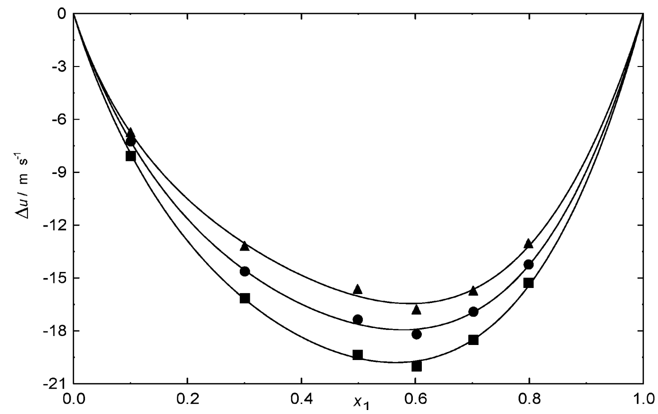

Figure 3. Δu for propan-1-ol + heptane mixtures at 60.79 MPa: (▲) 293.15 K; (●) 303.15 K; (■) 313.15 K; (—) calculated from the Redlich−Kister equation, $\Delta u = x_1(1 - x_1)\sum_{i=0}^{2} a_i(1 - 2x_1)^i$.

compressibility of heptane as the pressure increases because of the closer molecular packing in the alkane than that in both the alcohol and the alcohol containing mixtures.

The Δu isotherms are negative in the whole concentration range both at atmospheric pressure and at elevated pressures. The absolute values of Δu decrease with increasing pressure (Figure 2) and increase with decreasing temperature (Figure 3). Since the positive excess compressibility of alcohol + alkane mixtures under atmospheric pressure is believed to be due to the disruption of hydrogen bonds in the alcohol during mixing, the decrease of Δu with increasing pressure suggests that the interference of the alkane with the hydrogen bond structure of the alcohol becomes less effective at higher pressures.

Literature Cited

(1) Heydemann, P. L. M.; Houck, J. C. Self-consistent ultrasonic method for determination of the equation of state of liquids at very high pressures. *J. Appl. Phys.* **1969**, *40*, 609−613.

(2) Kell, G. S.; Whalley, E. Reanalysis of the density of liquid water in the range 0−150 °C and 0−1 kbar. *J. Chem. Phys.* **1975**, *62*, 3496−3503.

(3) Chen, C.-T.; Fine, R. A.; Millero, F. J. The equation of state of pure water determined from sound speeds. *J. Chem. Phys.* **1979**, *66*, 2142−2144.

(4) Sun, T. F.; Bominaar, S. A. R. C.; Ten Seldam, C. A.; Biswas, S. N. Evaluation of the thermophysical properties of toluene and*n*-heptane from 180 to 320 K and up to 260 MPa from speed-of-sound data. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 696−704.

(5) Marczak, W.; Dzida, M.; Ernst, S. Determination of the thermodynamic properties of 1-propanol and 1-hexanol from speed of sound measurements under elevated pressures. *High Temp.—High Pressures* **2000**, *32*, 283−292.

(6) Daridon, J. L.; Lagourette, B.; Grolier, J.-P. E. Experimental measurements of the speed of sound in *n*-hexane from 293 to 373 K and up to 150 MPa. *Int. J. Thermophys.* **1998**, *19*, 145−160.

(7) Junquera, S.; Tardajos, G.; Aicart, E. Speeds of sound and isentropic compressibilities of (cyklohexane + benzen) and (1-chlorobutane + *n*-hexane or + *n*-heptane or + *n*-octane or + *n*-decane) at 298.15 K. *J. Chem. Thermodyn.* **1988**, *20*, 1461−1467.

(8) Papaioannou, D.; Ziakas, D.; Panayiotou, C. Volumetric properties of binary mixtures. 1. 2-propanone + 2,2,4-trimethylpentane and *n*-heptane + ethanol mixtures. *J. Chem. Eng. Data* **1991**, *36*, 35−39.

(9) Kiyohara, O.; Benson, G. C. Ultrasonic speeds and isentropic compressibilities of *n*-alkanol + *n*-heptane mixtures at 298.15 K. *J. Chem. Thermodyn.* **1979**, *11*, 861−873.

(10) Muringer, M. J. P.; Trappeniers, N. J.; Biswas, S. N. The effect of pressure on the sound velocity and density of toluene and *n*-heptane up to 2600 bar. *Phys. Chem. Liq.* **1985**, *14*, 273−296.

(11) *TRC Databases for Chemistry and Engineering—Thermodynamic Tables*, Version 1998-2.d-1460, 1991; d-5000, 1966; Thermodynamic Research Center, Texas A&M University System: College Station, TX, 1998.

(12) Treszczanowicz, A. J.; Benson, G. C. Excess volumes for *n*-alkanols + *n*-alkanes I. Binary mixtures of methanol, ethanol, *n*-propanol, and *n*-butanol + *n*-heptane. *J. Chem. Thermodyn.* **1977**, *9*, 1189−1197.

(13) Aicart, E.; Costas, M.; Junquera, S.; Tardajos, G. Ultrasonic speeds and isentropic compressibilities of (1, 4 dioxane + *n*-heptane or *n*-decane or n-tetradecane). *J. Chem. Thermodyn.* **1990**, *22*, 1153−1158.

(14) Ormanoudis, C.; Dakos, C.; Panayiotou, C. Volumetric properties of binary mixtures. 2. Mixtures of *n*-hexane with ethanol and 1-propanol. *J. Chem. Eng. Data* **1991**, *36*, 39−42.

(15) Marks, G. W. *J. Acoust. Soc. Am.* **1967**, *41*, 103 quoted by Kiyohara, O., Benson, G. C. Ultrasonic speeds and isentropic compressibilities of *n*-alkanol + *n*-heptane mixtures at 298.15 K. *J. Chem. Thermodyn.* **1979**, *11*, 861−873.

(16) Jiménez, E.; Franjo, C.; Segade, L.; Legido, J. L.; Paz Andrade, M. I. Excess molar enthalpies for di-*n*-butyl ether + 1-propanol + *n*-octane at 298.15K. *Fluid Phase Equilib.* **1997**, *133*, 179−185.

(17) Fernandez, J.; Berro, C.; Paz Andrade, M. I. Excess thermodynamics functions of 1-propanol + methyl propanoate and 1-propanol + methyl butanoate systems. *Fluid Phase Equilib.* **1985**, *20*, 145−153.

(18) Haraschta, P.; Heintz, A.; Lehmann, J. K.; Peters, A. Excess molar volumes and viscosities of binary mixtures of 4-methylpyridine with methanol, ethanol, propan-1-ol, propan-2-ol, butan-2-ol, and 2-methylpropan-2-ol at 298.15 K and atmospheric pressure. *J. Chem. Eng. Data* **1999**, *44*, 932−935.

(19) Żak, A.; Dzida, M.; Zorębski, M.; Ernst, S. A high-pressure device for measurements of the speed of sound in liquids. *Rev. Sci. Instrum.* **2000**, *71*, 1756−1765.

(20) Marczak, W. Water as a standard in the measurements of speed of sound in liquid. *J. Acoust. Soc. Am.* **1997**, *102*, 2776−2779.

(21) Sun, T.; Biswas, S. N.; Trappeniers, N. J.; Ten Seldam, C. A. Acoustic and thermodynamic properties of methanol from 273 to 333 K and at pressures to 280 MPa. *J. Chem. Eng. Data* **1988**, *33*, 395−398.

(22) Hawley, S.; Allegra, J.; Holton, G. Ultrasonic-absorption and sound-speed data for nine liquids at high pressures. *J. Acoust. Soc. Am.* **1970**, *47*, 137−143.

(23) *Landolt-Börnstein*; Hellwege, K. H., Ed.; Numerical Data and Functional Relationships in Science and Technology, Springer-Verlag: Berlin-Heidelberg-New York, 1967; Group II, Atomic and molecular physics, Volume 5 Molecular Acoustics.

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