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Thermodynamic properties of mixtures of *N*-methyl-2-pyrrolidinone and methanol at temperatures between 298.15 K and 343.15 K and pressures up to 60 MPa

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ABSTRACT

We report measurements of the speed of sound in mixtures of *N*-methyl-2-pyrrolidinone and methanol at temperatures between 298.15 K and 343.15 K and at pressures up to 60 MPa. The measurements were made using a dual path pulse-echo apparatus operating at a frequency of 5 MHz. We have also measured the isobaric specific heat capacity of each mixture as a function of temperature at ambient pressure, by means of a Setaram DSC III microcalorimeter. The experimental results have been combined with literature data for the density of the same mixtures as a functions of temperature at ambient pressure to obtain the density, isobaric specific heat capacity, and other thermodynamic properties at temperatures between 298.15 K and 343.15 K and at pressures up to 60 MPa. Detailed comparisons with the literature data are presented.

1. Introduction

The *N*-methyl-2-pyrrolidinone (NMP, C_5H_9NO, Chemical Abstracts number 872-50-4) is a dipolar aprotic compound that is miscible with water, lower alkanols and many other common organic solvents. It has good thermal and chemical stability, and low volatility. It has applications as a solvent in various processes including polymer synthesis, extractive distillation, and desulfurization of fuels [1]; it also occurs as an intermediate in many synthesis processes. Mixtures of NMP and methanol are frequently used to obtain enhanced solvent properties. Thermodynamic properties of this mixed solvent system over relevant ranges of temperatures and pressures are useful for the design and optimisation of industrial processes.

Various thermodynamic properties of (NMP + alkanol) have been reported over a wide range of temperatures at ambient pressure [2–8], and the density has been measured at elevated pressure [9]. The system is highly non-ideal, no doubt as a result of specific interactions and differences in molecular size and shape. The present work greatly extends these earlier studies by providing a consistent set of both caloric and thermal properties over the full composition range and over a significant temperature range with pressures up to 60 MPa. The results obtained in this study will permit equations of state, or other thermodynamic models, for associating fluids to be tested in a more stringent manner than is the case with density data alone.

In the present work, we used sound speed measurements to characterise the properties of the mixture, for various fixed compositions, over a range of temperatures and pressures. A numerical integration method was then used to determine the thermal and caloric properties of each composition studied by combining the speed of sound $u(T,p)$ with the density $\rho_0(T)$ and isobaric specific heat capacity $c_{p,0}(T)$ of the same mixture composition along the isobar at ambient pressure. This approach, which is based on exact thermodynamic relationships, was first devised by Davis and Gordon and applied to mercury [10]. Since then, many other workers have applied the same fundamental approach, with refined numerical methods, to a wide range of liquids [11–14].

2. Experimental

The sources and mole-fraction purities x of the chemical used are as follows: NMP ($x \geqslant 0.999$), methanol ($x \geqslant 0.999$) and *n*-octane ($x \geqslant 0.999$) were obtained from Fluka; methylbenzene ($x \geqslant 0.998$) and 1-butanol ($x \geqslant 0.995$) were obtained from Sigma–Aldrich. All of liquids were stored over 0.4 nm molecular sieves, out of light, and degassed, either with ultrasound or by boiling under reflux, before use.

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The ultrasonic cell used to measure the speed of sound is shown in figure 1 [15,16]. The main elements of the cell were a pair of reflectors between which a piezoelectric disc transducer was held by means of a pair of clamping rings and two tubular spacers of unequal length. These pieces were held together by three threaded rods, of 2 mm diameter, that passed through clearance holes located at an angle of $2\pi/3$ to each other in the clamping rings and the reflectors. A further set of holes provided in each piece was used to aid filling and evacuation of the cell.

The transducer (10 mm diameter, 0.4 mm thickness) used was made from lead zirconate titanate plated on both major faces with gold; it was operated at its resonant frequency of 5 MHz. The two hollow cylindrical spacers were, respectively, 20 mm and 30 mm in length, and their inside and outside diameters were 18 mm and 22 mm, respectively. They were ground from solid pieces of fused quartz such that the lengths were accurate to ±10 μm, and the ends were flat and parallel to better than ±2.5 μm. An advantage of using fused quartz is that its thermal expansion coefficient is very small so that corrections required to the path lengths as the temperature was changed were negligible. The stainless-steel clamping rings were of identical dimensions and hence made no contribution to the difference between the path lengths in the two parts of the cell at any temperature or pressure. A further feature of the cell was that the reflectors, which were 10 mm deep and 25 mm in diameter, each had a conical cavity in the rear face. The reason for this cavity was to disperse sound that passed into the reflector and was then reflected from the rear face.

The transducer was energised with a single five-cycle tone burst at 5 MHz, with an amplitude of 20 V peak-to-peak, thereby causing ultrasonic pulses to propagate into the fluid to either side; these pulses were reflected at the ends of the cell and detected when they returned to the transducer. The signal generated by the transducer was digitised at a sampling rate of 200 MHz by a digital oscilloscope and the data transferred to a computer for analysis in software. The speed of sound u was determined from the difference Δt between the arrival times of the two returning echoes and the difference ΔL between the path lengths to either side of the transducer by means of the simple relation:

$$u = 2\Delta L/\Delta t. \tag{1}$$

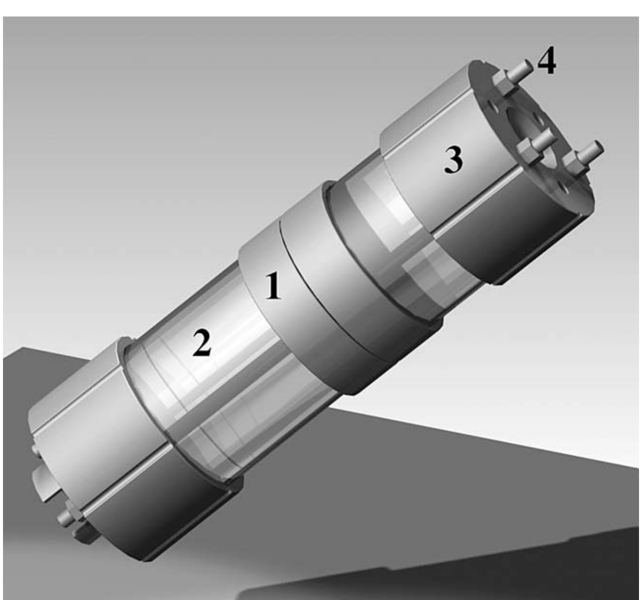

FIGURE 1. The ultrasonic cell: 1, stainless-steel clamping ring; 2, fused quartz spacer tube; 3, reflector with conical rear cavity; and 4, threaded rod and nut.

TABLE 1

Experimental speeds of sound u for {xNMP + (1 − x) CH_3OH} at pressures p and temperatures T

T = 298.15 K		T = 313.15 K		T = 328.15 K		T = 343.15 K	
p/MPa	u/(m · s^{-1})	p/MPa	u/(m · s^{-1})	p/MPa	u/(m · s^{-1})	p/MPa	u/(m · s^{-1})
			x = 0.0000				
0.135	1101.54	0.091	1052.16	0.165	1004.54	0.165	955.98
0.998	1106.68	1.000	1057.68	1.000	1009.57	1.001	962.46
4.999	1129.63	5.000	1082.08	5.000	1037.06	4.999	991.03
10.002	1156.87	10.002	1112.22	10.001	1068.09	10.007	1025.26
15.002	1183.02	15.000	1140.22	14.999	1097.73	15.001	1056.11
19.991	1209.29	20.001	1166.96	19.998	1126.25	19.997	1086.84
24.996	1233.36	25.001	1192.16	25.000	1153.31	25.000	1114.77
29.991	1257.23	30.003	1217.37	29.999	1179.29	30.002	1141.60
34.998	1279.19	35.000	1241.00	34.998	1203.23	34.992	1166.37
40.002	1301.09	39.999	1263.57	39.994	1226.30	40.002	1192.24
45.002	1322.89	44.999	1287.40	44.998	1249.50	45.000	1215.98
50.004	1342.30	49.998	1306.62	50.000	1271.59	50.004	1237.64
54.997	1361.36	54.997	1326.41	54.999	1293.23	55.000	1260.49
59.998	1380.97	59.999	1346.82	59.990	1312.61	60.002	1281.74
			x = 0.2016				
0.129	1277.13	0.117	1228.17	0.109	1173.93	0.106	1121.82
1.000	1281.18	1.012	1232.30	1.000	1177.70	1.003	1125.88
4.997	1299.35	5.002	1249.48	4.998	1197.97	4.999	1147.31
9.997	1321.51	10.005	1273.55	9.992	1221.18	9.989	1173.31
14.993	1343.53	15.000	1295.24	14.987	1246.07	14.987	1199.46
19.997	1365.85	19.998	1317.68	20.003	1270.00	19.995	1224.20
24.998	1386.05	24.999	1339.13	24.998	1292.80	24.996	1248.06
29.993	1406.37	29.998	1359.45	29.994	1314.72	29.996	1270.86
34.990	1426.29	34.988	1379.93	34.996	1336.96	34.989	1292.86
39.995	1444.70	39.991	1399.59	39.993	1357.22	39.992	1314.78
44.995	1463.60	44.996	1419.31	44.994	1376.69	44.989	1335.69
50.004	1481.91	49.978	1437.54	49.988	1396.73	49.992	1356.36
54.994	1499.57	54.997	1457.62	54.979	1415.87	54.987	1375.80
60.001	1516.51	59.987	1474.91	59.999	1433.50	59.988	1394.36
			x = 0.3982				
0.130	1386.21	0.107	1334.87	0.132	1277.45	0.122	1227.79
1.000	1390.04	1.003	1337.53	1.007	1282.32	0.999	1229.29
4.992	1406.04	4.996	1352.79	4.993	1297.17	4.999	1246.75
9.984	1424.43	9.998	1372.59	9.990	1319.23	9.998	1269.49
14.985	1444.86	14.983	1392.50	14.993	1340.27	14.998	1291.43
19.986	1464.28	19.993	1412.01	19.984	1361.99	19.991	1314.14
25.000	1483.15	24.996	1432.59	24.995	1383.49	24.995	1338.55
29.984	1500.83	29.996	1452.20	29.986	1402.74	29.993	1357.02
34.990	1518.94	34.990	1470.22	34.982	1421.54	34.987	1376.94
40.000	1536.91	39.995	1488.14	39.986	1440.85	39.982	1396.01
44.985	1554.10	44.999	1505.94	44.991	1459.63	44.992	1416.11
49.996	1570.47	49.996	1523.59	49.990	1477.83	49.994	1433.73
54.993	1585.93	54.995	1540.49	54.992	1495.12	54.978	1452.33
59.994	1602.33	59.966	1557.16	59.999	1512.21	59.988	1470.34
			x = 0.4931				
0.131	1424.50	0.102	1371.27	0.102	1315.01	0.127	1258.51
0.999	1427.52	1.030	1374.07	0.993	1317.59	0.997	1261.66
5.002	1441.82	5.001	1389.22	5.004	1333.26	5.003	1279.24
10.027	1460.63	10.003	1407.65	9.991	1353.84	10.010	1301.51
15.010	1478.86	15.007	1427.58	15.002	1374.60	15.002	1323.71
19.995	1496.99	20.009	1447.06	20.015	1395.05	19.994	1344.88
24.999	1516.14	25.006	1464.94	24.992	1414.62	25.001	1365.83
30.000	1533.45	29.996	1483.27	29.995	1433.74	29.995	1385.53
35.011	1550.56	34.996	1500.95	35.005	1452.33	34.998	1405.81
40.004	1567.46	39.993	1519.62	39.995	1471.41	40.008	1425.18
45.002	1584.72	45.014	1537.01	44.997	1488.80	45.003	1443.03
50.004	1600.46	49.994	1553.01	50.016	1507.74	50.007	1461.87
55.000	1617.17	54.995	1569.95	55.000	1523.70	55.010	1480.11
59.999	1632.25	60.007	1586.02	59.992	1540.00	60.006	1496.60
			x = 0.5889				
0.132	1454.35	0.103	1400.84	0.104	1343.10	0.109	1289.93
1.000	1458.03	1.003	1404.75	1.012	1345.77	1.003	1293.23
4.993	1471.87	4.998	1419.09	4.986	1361.20	4.996	1309.17
10.001	1489.83	9.991	1437.30	9.991	1380.77	10.000	1329.87
15.006	1507.67	14.985	1454.41	14.994	1400.91	15.004	1351.24
19.982	1525.36	19.992	1473.55	19.997	1420.65	19.989	1370.52
24.976	1542.29	24.989	1491.54	24.989	1439.93	24.989	1391.32