Speed of Ultrasound, Density, and Adiabatic Compressibility for 3-Methylpyridine + Heavy Water in the Temperature Range 293−313 K

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The speed of ultrasound and density for 3-methylpyridine (1) + heavy water (2) were measured within the whole concentration range and at temperatures from 293 to 313 K. Smoothing polynomials approximating the dependencies of speed and density on temperature were determined. The speeds of sound, densities, and adiabatic compressibilities (calculated using the Laplace formula) were plotted as functions of the mole fraction x_1. The speed of sound and compressibility isotherms show single extrema and nearly common crossing points at low 3-methylpyridine concentrations, while the density decreases monotonically with increasing x_1.

Introduction

The phase behavior of 3-methylpyridine (1) + heavy water (2) was studied by Cox (1952) who found a closed miscibility gap with the lower and upper consolute temperatures $t = 38.5$ °C (at the mole fraction $x_1 = 0.077$) and $t = 117$ °C (at $x_1 = 0.100$), respectively. The results of other experimental studies and theoretical predictions are close to that finding (Larsen and Sorensen, 1985; Sorensen and Larsen, 1985).

The appearance or, at least, an expansion of a closed miscibility gap is observed in many liquid water−organic mixtures when H_2O is replaced by D_2O. 2- and 3-methylpyridine are completely miscible with water, while their mixtures with heavy water show closed miscibility gaps. For aqueous solutions of 2,4-, 2,5-, and 2,6-dimethylpyridine (lutidine), the replacement of H_2O by D_2O leads to a decrease of the lower critical solution temperatures, while the upper ones increase for the 2,4- and 2,5-dimethylpyridine solutions and remains unchanged for the 2,6-dimethylpyridine solution (Andon and Cox ,1952; Cox, 1952; Sorensen and Larsen, 1985). This phenomenon is often interpreted in terms of hydrogen bonding and structural features of water and aqueous solutions.

This study was focused mainly on the compressibility of the 3-methylpyridine (1) + heavy water (2) system. Since the phase behavior of this system is similar to that of 2,6-dimethylpyridine + water, the present study may be considered to be an extension of an earlier one (Ernst et al., 1996).

Experimental Section

Chemicals. 3-Methylpyridine (Aldrich, 99%) was purified by distillation. Its density and refractive index at 20 °C were $\rho = 956.45$ kg m^{-3} and $n_D = 1.5065$, respectively (literature data: 956.4 kg m^{-3} and 1.5049, Beschke and Kleeman, 1980; 956.58 kg m^{-3} and 1.50682, Biddiscombe et al., 1954). The water content of 0.14% by mass, determined by the Karl Fischer method, may increase the density and speed of sound for 3-methylpyridine by ca. 0.20 kg m^{-3} and 0.83 m s^{-1}, respectively, as results from the data given by Ernst et al. (1994).

Safety Note. 3-Methylpyridine is flammable. It is harmful when inhaled, when in contact with skin, and if swallowed and is irritating to the eyes and the respiratory system.

The purity of heavy water (Sigma 99.9%) was checked by comparing its densities at (20, 25, 30, 35, and 40) °C with those calculated from the polynomial given by Kell (1972). The differences did not exceed 5 × 10^{-2} kg m^{-3}; i.e., they remained within the limits of the measurements accuracy. Heavy water is a hygroscopic liquid. Mixtures were prepared by mass and stored in sealed flasks.

Speed of Sound and Density Measurements. The group speed of sound at $f = 4$ MHz was measured by the sing-around technique (e.g., Hall and Yeager, 1973), using an apparatus designed and constructed at our laboratory (electronic part) and at the Institute of Fundamental Technical Research of the Polish Academy of Sciences, Warsaw (sample cell). The measurement accuracy can be estimated to be ±0.5 m s^{-1} while the precision depends on the difference between the measured speed of sound and that in a standard liquid (deionized water with electrolytic conductivity 0.6 × 10^{-4} S m^{-1}) and varies from (0.05 to 0.30) m s^{-1}.

The densities of the solutions were measured with a 25 cm^3 bicapillary pycnometer calibrated with the same water as the velocimeter; the accuracy of the density measurements was 5 × 10^{-2} kg m^{-3}.

The temperature was defined according to the IPTS-68, but as results from the analysis of errors, the effects caused by the difference between the temperature scales (IPTS-68 and ITS-90) are neglible.

The details concerning the speed of sound and density measurements were given in a previous paper (Ernst et al., 1996).

Results

The speeds of sound and densities for 3-methylpyridine + heavy water, measured for the whole concentration range within the temperatures 293 K to 313 K in about 5 K steps, are given in Table 1. The dependencies of the speed and density on temperature were approximated by the following parabolic ($n = 2$) or linear ($n = 1$) equations:

$$y = \sum_{i=0}^{n} a_i (T/\mathrm{K} - 293.15)^i \tag{1}$$

where y is the speed of sound (u) or density (ρ) and a_i ($a_i = u_i$ or $a_i = \rho_i$ for the speed of sound and density, respectively) are the polynomial coefficients given in Table 2 and

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Table 1. Speeds of Ultrasound (u) and Densities (ρ) for 3-Methylpyridine (1) + Heavy Water (2), Measured with a Sing-Around Velocimeter and a Bicapillary Pycnometer, Respectively[a]

x_1	T/K	u/m s^{-1}	T/K	u/m s^{-1}	T/K	u/m s^{-1}	T/K	u/m s^{-1}	T/K	u/m s^{-1}	T/K	ρ/kg m^{-3}	T/K	ρ/kg m^{-3}	T/K	ρ/kg m^{-3}	T/K	ρ/kg m^{-3}	T/K	ρ/kg m^{-3}
0.0150	293.11	1429.21	298.18	1438.81	302.92	1446.37	307.98	1453.02	312.98	1458.20	293.11	1098.00	298.13	1096.62	303.22	1095.09	308.23	1093.09	313.17	1090.93
0.0296	293.11	1450.46	298.18	1456.32	302.93	1460.60	307.99	1463.90	312.99	1465.99	293.11	1091.72	298.13	1089.43	303.23	1087.08	308.26	1084.76	313.24	1082.31
0.0375	293.12	1458.69	298.15	1462.80	302.88	1465.49	307.94	1467.19	312.92	1467.74	293.12	1088.24	298.16	1085.70	303.25	1083.17	308.25	1080.64	313.15	1077.86
0.0523	293.09	1470.81	298.14	1472.18	302.90	1472.39	307.97	1471.49			293.11	1082.32	298.20	1079.45	303.29	1076.69	308.24	1073.75		
0.0577	293.12	1475.31	298.17	1475.55	302.91	1474.76	307.97	1472.84			293.11	1079.47	298.16	1076.91	303.25	1074.43	308.16	1071.88		
0.0789	293.11	1489.65	298.16	1486.52	302.90	1482.69	307.95	1477.64			293.17	1072.11	298.14	1068.85	303.23	1065.74	308.23	1063.03		
0.1423	293.11	1521.24	298.18	1511.28	302.92	1501.50	307.98	1490.60	312.98	1479.40	293.13	1053.80	298.13	1049.91	303.26	1045.90	308.24	1041.95	313.20	1037.73
0.1987	293.09	1537.09	298.14	1523.33	302.87	1510.22	307.92	1496.01	312.91	1481.74	293.12	1041.78	298.19	1037.66	303.23	1033.52	308.26	1028.92	313.24	1024.52
0.3042	293.13	1545.37	298.15	1528.20	302.90	1511.80	307.95	1494.33	312.94	1476.90	293.12	1022.23	298.16	1017.69	303.22	1013.21	308.17	1008.67	313.15	1003.89
0.3910	293.11	1538.52	298.16	1519.79	302.88	1502.16	307.93	1483.25	312.91	1464.57	293.16	1011.00	298.12	1006.42	303.09	1001.83	308.23	996.77	313.17	991.76
0.6023	293.10	1500.94	298.14	1481.16	302.87	1462.57	307.90	1442.93	312.90	1423.35	293.23	987.40	298.23	982.69	303.29	978.05	308.22	973.33	313.21	968.45
0.7867	293.11	1468.75	298.14	1448.78	302.86	1430.07	307.91	1410.16	312.88	1390.60	293.17	969.50	298.17	965.21	303.22	960.44	308.20	956.00	313.11	951.22
1	293.07	1443.72	298.10	1423.08	302.83	1403.76	307.88	1383.34	312.86	1363.32	293.09	956.52	298.24	951.75	303.20	947.19	308.29	942.50	313.20	937.97

[a] The lack of some data at $T > 312$ K results from the phase separation of the system.

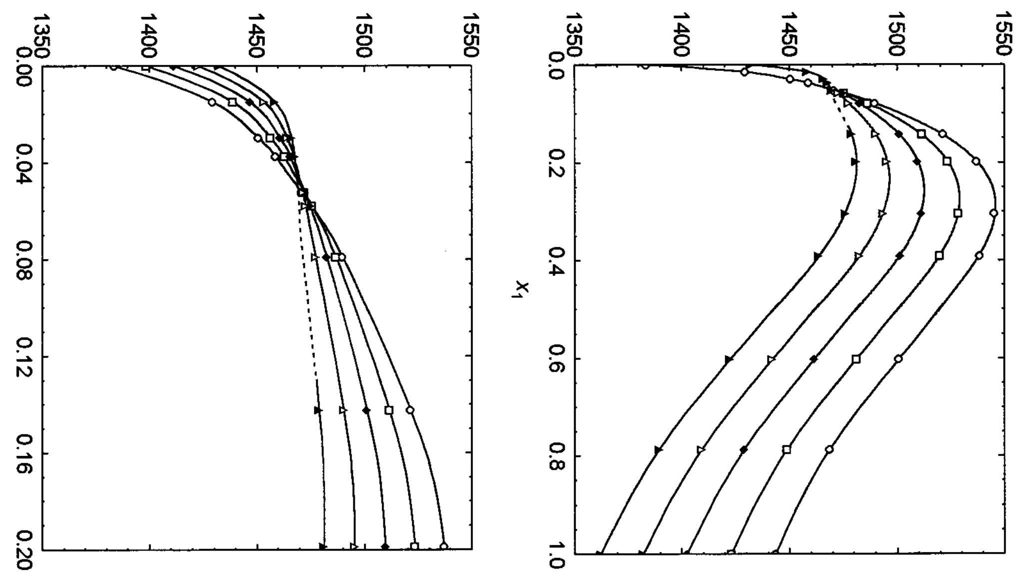

Figure 1. Speed of sound isotherms for 3-methylpyridine (1) + heavy water (2): (○) 293.15 K; (□) 298.15 K; (◆) 303.15 K; (△) 308.15 K; (▲) 313.15 K; (top) in the whole concentration range (some points were omitted for clarity); (bottom) in dilute solutions. In the phase separation range of concentration, a hypothetical isotherm is given by the dotted line.

calculated by the least squares method. As the criterion to choose between the linear and parabolic functions, the mean deviations from the regression lines were applied. In all the following calculations the u and ρ values calculated from eq 1 were used.

For the pure heavy water the densities were calculated from the polynomial given by Kell (1972) and the speed of sound from the following function (Marczak, 1996):

$$u/\text{m s}^{-1} = 1300.87 + 5.1541t/°\text{C} - 0.05535(t/°\text{C})^2 + 2.1397 \times 10^{-4}(t/°\text{C})^3 \quad (2)$$

The speed of sound and density isotherms are plotted in Figures 1 and 2, respectively.

The coefficient of the adiabatic compressibility, κ_S, was calculated from the Laplace formula:

$$\kappa_S = 1/\rho u^2 \quad (3)$$

The isotherms $\kappa_S(x_1)$ are plotted in Figure 3.

Summary

The features of the speed of sound, density, and adiabatic compressibility isotherms for 3-methylpyridine (1) + heavy

Table 2. Coefficients of the Speed of Ultrasound (u) and Density (ρ) Polynomials (1) for 3-Methylpyridine (1) + Heavy Water (2) for Temperatures within 293 K ÷ T_{max} (T_{max} = 308 K for 0.05 < x_1 < 0.08 and T_{max} = 313 K for All the Other Concentrations) and Mean Deviations from the Regression Lines δ_u and δ_ρ

x_1	u_0/m s^{-1}	u_1/m s^{-1} K^{-1}	u_2/m s^{-1} K^{-2}	δ_u/m s^{-1}	ρ_0/kg m^{-3}	ρ_1/kg m^{-3} K^{-1}	ρ_2/kg m^{-3} K^{-2}	δ_ρ/kg m^{-3}
0.0150	1429.31	2.0296	−0.028 92	0.03	1097.97	−0.2311	−0.006 04	0.06
0.0296	1450.53	1.2720	−0.024 86	0.03	1091.69	−0.4451	−0.001 04	0.03
0.0375	1458.73	0.9266	−0.023 84	0.03	1088.19	−0.4772	−0.001 85	0.08
0.0523	1470.83	0.3828	−0.022 82	0.01	1082.31	−0.5637		0.07
0.0577	1475.31	0.1565	−0.021 83	0.01	1079.45	−0.5023		0.04
0.0789	1489.63	−0.5234	−0.019 34	0.00	1072.13	−0.6907	0.005 75	0.03
0.1423	1521.17	−1.9235	−0.009 24	0.01	1053.76	−0.7535	−0.002 20	0.07
0.1987	1536.93	−2.7015	−0.004 62	0.01	1041.76	−0.7933	−0.003 29	0.09
0.3042	1545.31	−3.4117	−0.002 31	0.02	1022.17	−0.8700	−0.002 11	0.07
0.3910	1538.37	−3.7101	−0.001 24	0.03	1010.98	−0.8897	−0.003 48	0.05
0.6023	1500.76	−3.9345	0.000 79	0.03	987.44	−0.9142	−0.001 55	0.06
0.7867	1468.58	−3.9781	0.002 34	0.01	969.54	−0.8676	−0.002 50	0.12
1	1443.41	−4.1223	0.002 98	0.01	956.45	−0.9212		0.01

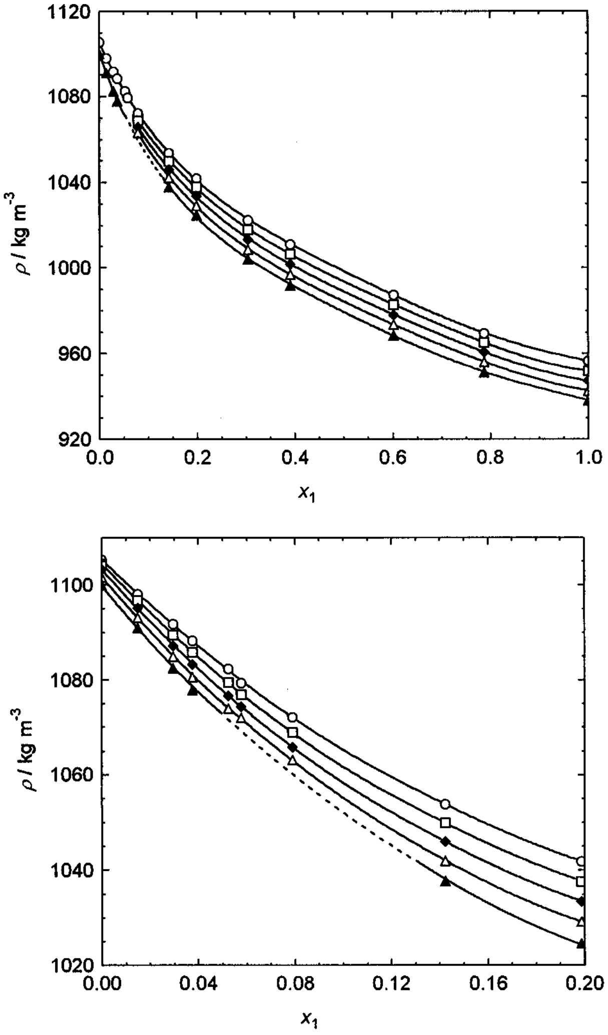

Figure 2. Density isotherms for 3-methylpyridine (1) + heavy water (2): symbols as in Figure 1; (top) in the whole concentration range (some points were omitted for clarity); (bottom) in dilute solutions. In the phase separation range of concentration, a hypothetical isotherm is given by the dotted line.

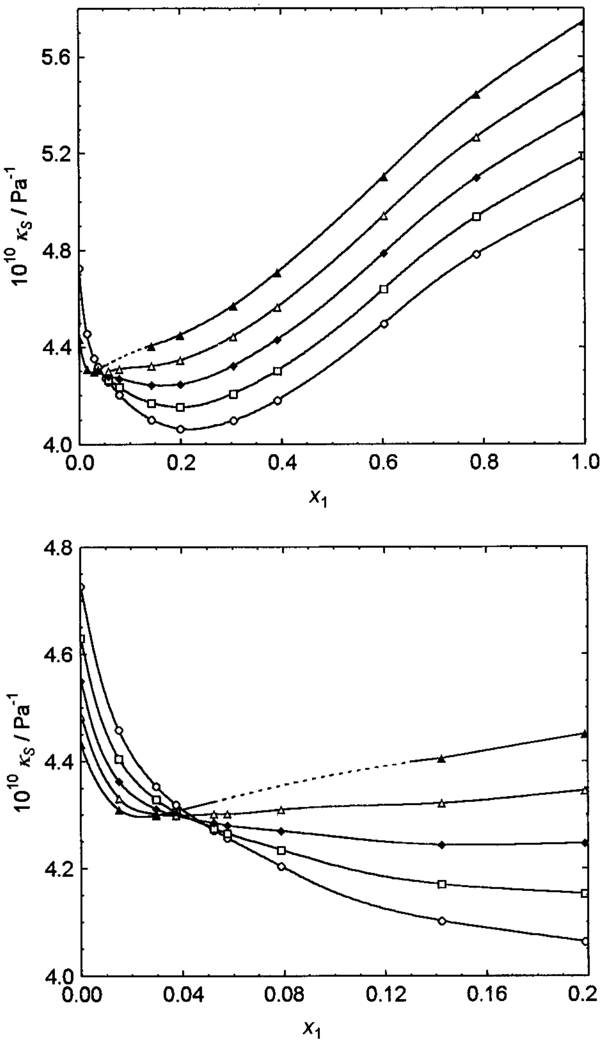

Figure 3. Adiabatic compressibility isotherms for 3-methylpyridine (1) + heavy water (2): symbols as in Figure 1; (top) in the whole concentration range (some points were omitted for clarity); (bottom) in dilute solutions. In the phase separation range of concentration, a hypothetical isotherm is given by the dotted line.

water (2) are similar to those for 2,6-dimethylpyridine + water (Ernst et al., 1996). The density decreases monotonically with increasing concentration of 3-methylpyridine (Figure 2), while the speed of sound and compressibility isotherms show maxima and minima, respectively (Figures 1 and 3). Both the u and κ_S isotherms cross each other at $x_1 \approx 0.05$. With increasing temperature the extrema flatten and move toward lower concentrations of 3-methylpyridine; the crossing points shift slightly in the same direction.

Similar crossing points and extrema of the speed of sound and compressibility isotherms were observed for aqueous solutions of 2- and 4-methylpyridine (Ernst and Marczak, 1995, 1992). According to Kaulgud and Patil (1975), these extrema are typical of aqueous solutions of amines. Furthermore, it seems to be likely that the approximate common crossing points of the u and κ_S isotherms are also characteristic of the mixtures of amines with water and heavy water.

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