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Speed of Ultrasound, Density, and Adiabatic Compressibility for 2-Methylpyridine + Heavy Water in the Temperature Range 293 K to 313 K

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The speed of ultrasound and density for 2-methylpyridine (1) + heavy water (2) were measured at atmospheric pressure and at temperatures ranging from 293 K to 313 K over the entire composition range. Parabolic equations approximating the dependencies of speed and density on temperature were determined. The adiabatic compressibility was calculated from the Laplace formula. The speed of sound, density, and compressibility isotherms were plotted as functions of the mole fraction x_1. The density decreases monotonically with increasing 2-methylpyridine concentration, while both the speed and compressibility isotherms show single extrema (maxima and minima, respectively). The speed of sound and compressibility isotherms cross one another in a narrow concentration interval in the vicinity of $x_1 \approx 0.04$. The mixture of 3-methylpyridine with heavy water shows similar features although its phase properties differ from those of the 2-methylpyridine solution.

Introduction

The adiabatic compressibilities of binary water−organic mixtures have been investigated extensively in various laboratories, while the data for deuterium oxide solutions of organic compounds are rather scarce. Because the isotopic substitution of water is a powerful tool for investigating the solvation mechanism in aqueous solutions of nonelectrolytes (Marcus and Ben-Naim, 1985), reliable experimental results for both binary H_2O and D_2O mixtures can be effectively applied for this purpose. Aqueous solutions of 2-, 3-, and 4-methylpyridine, as well as the mixture of 3-methylpyridine with D_2O, were investigated in our laboratory earlier (Ernst and Marczak, 1992, 1995; Marczak and Ernst, 1998; Marczak, 1996). Both this study, dealing with the 2-methylpyridine (1) + D_2O (2) system, and another one, carried out at present and devoted to 4-methylpyridine + D_2O, may be regarded as a continuation of our previous studies.

The most interesting features of the adiabatic compressibility ($\kappa_S = -1/V(\partial V/\partial p)_S$) of typical binary aqueous nonelectrolyte solutions seem to be deep, but flat, minima of the isotherms at relatively low concentrations of the nonelectrolyte, and crossing of those isotherms at even lower concentrations in a very narrow concentration interval (e.g. for ethanol (1) + water (2) solutions the corresponding mole fractions are $x_1 \approx 0.1$ and $x_1 \approx 0.05$; Conde et al., 1982; Jerie et al., 1986). This crossing interval, sometimes mentioned as a common crossing point (e.g. Gutmann and Resch, 1995), results from the very flat minimum of the $\kappa_S(T)$ function at $x_1 \approx 0.05$. In an earlier work (Marczak, 1996), similar maxima and crossing points were reported for the 3-methylpyridine + heavy water mixture.

The aim of this study was to provide reliable data for the comparison of mixtures of methylpyridine isomers with light and heavy water.

Table 1. Density ρ and Refractive Index n_D of 2-Methylpyridine at T = 298.15 K, and the Mole Fraction of Water, x, Determined by the Karl Fischer Method

	exp	lit.
ρ/(kg m^{-3})	939.42 ± 0.05	939.6[a]
n_D	1.4975 ± 0.0002	1.4980[b]
100x	0.36 ± 0.03	

[a] Das et al. (1993); critically evaluated value based on experimental data published by various authors. [b] Sacconi et al. (1960).

Experimental Section

Chemicals. 2-Methylpyridine (Aldrich, 98% by mass) was purified by distillation in a rectifying column. Its density, refractive index, and water content, determined by Karl Fischer titration, are given in Table 1. The small discrepancies between the experimental data and the literature ones result probably from differences in the concentrations of water and 4-methylpyridine that commonly contaminate "pure" 2-methylpyridine.

Heavy water (from Sigma) was used without any pretreatment. Its density, 1103.75 kg m^{-3} at 298.15 K, is a little lower than that reported by Kell (1977) (1104.45 kg m^{-3}), most probably because of the presence of H_2O. The isotopic purity of the heavy water, estimated from the density data assuming thermodynamic ideal mixing of D_2O with H_2O, is 99.35 mol %. This value is close to the value 99.45 mol % calculated both from the speeds of sound in pure H_2O and D_2O (Marczak, 1997a,b) and from the polynomial of Kiyohara et al. (1977) which approximates the deviation of the speed of sound from additivity on a mole fraction scale. The solutions were prepared by mass using an analytical balance and stored in sealed flasks. Since the densities of the mixture components are close to one another, the corrections for weighing in air were neglected.

From the balance accuracy (±6 × 10^{-4} g), the uncertainty in the mole fraction of the solution was estimated to be 5

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Table 2. Speeds of Ultrasound (u) in 2-Methylpyridine (1) + Heavy Water (2) Measured with the Pulse−Echo−Overlap Apparatus

x_1	t/°C	u/(m s^{-1})	t/°C	u/(m s^{-1})	t/°C	u/(m s^{-1})	t/°C	u/(m s^{-1})	t/°C	u/(m s^{-1})
0.0000	20.19	1384.78	25.22	1399.56	29.59	1411.07	34.63	1422.74	40.66	1434.36
0.0200	20.19	1445.83	25.23	1453.32	29.60	1458.87	34.64	1464.03	40.69	1468.52
0.0404	20.20	1476.30	25.23	1478.83	29.60	1480.26	34.63	1480.99	40.68	1480.38
0.0484	20.22	1484.83	25.25	1485.75	29.62	1485.89	34.66	1485.18	40.74	1482.93
0.0593	20.21	1495.01	25.23	1493.97	29.60	1492.44	34.64	1489.93	40.72	1485.56
0.0776	20.23	1509.25	25.27	1505.22	29.63	1501.28	34.68	1496.08	40.74	1488.66
0.0995	20.16	1522.73	25.18	1515.73	29.52	1509.43	34.50	1501.60	40.52	1491.11
0.1858	20.19	1550.94	25.23	1536.92	29.60	1524.57	34.62	1510.22	40.64	1492.52
0.2958	20.18	1552.99	25.15	1535.30	29.44	1520.15	34.44	1502.28	40.47	1480.34
0.4062	20.19	1537.68	25.22	1517.82	29.59	1500.61	34.60	1480.96	40.61	1457.19
0.5002	20.24	1515.25	25.21	1494.96	29.52	1477.59	34.50	1457.40	40.48	1433.00
0.5923	20.19	1490.05	25.22	1469.34	29.59	1451.51	34.60	1431.19	40.61	1406.79
0.7044	20.16	1458.76	25.17	1438.34	29.49	1420.90	34.48	1400.74	40.49	1376.39
0.7981	20.20	1436.37	25.22	1415.75	29.58	1398.06	34.58	1377.94	40.62	1353.72
0.9008	20.23	1415.82	25.22	1395.15	29.53	1377.57	34.52	1357.29	40.57	1332.75
1.0000	20.21	1400.05	25.18	1379.18	29.47	1361.42	34.45	1340.95	40.45	1316.47

Table 3. Densities (ρ) of 2-Methylpyridine (1) + Heavy Water (2) Measured with the Vibrating-Tube Densimeter

x_1	t/°C	ρ/(kg m^{-3})	t/°C	ρ/(kg m^{-3})	t/°C	ρ/(kg m^{-3})	t/°C	ρ/(kg m^{-3})	t/°C	ρ/(kg m^{-3})
0.0000	19.98	1104.60	25.03	1103.80	29.97	1102.53	34.95	1101.08	40.27	1099.12
0.0200	19.99	1095.57	24.99	1093.79	30.04	1091.93	34.87	1089.66	40.17	1087.17
0.0404	19.99	1087.08	24.99	1084.76	30.04	1082.36	34.87	1079.84	40.17	1076.83
0.0484	19.97	1083.75	24.98	1081.46	29.97	1078.98	35.05	1076.09	40.19	1073.18
0.0593	19.97	1079.76	24.98	1077.27	29.97	1074.55	35.05	1071.46	40.20	1068.21
0.0776	19.96	1073.61	25.03	1070.67	30.07	1067.45	35.11	1064.22	40.15	1060.85
0.0995	19.98	1066.78	24.99	1063.48	29.97	1060.07	34.93	1056.58	40.25	1052.58
0.1858	19.99	1046.10	24.99	1041.63	30.05	1037.28	34.86	1033.00	40.18	1028.31
0.2958	19.98	1025.50	24.99	1020.93	29.97	1016.22	34.93	1011.45	40.25	1006.22
0.4062	19.99	1008.87	24.99	1003.84	30.05	998.84	34.86	993.98	40.19	988.61
0.5002	19.98	995.29	24.99	990.59	29.97	985.71	34.93	980.87	40.25	975.42
0.5923	19.99	983.69	24.99	978.63	30.05	973.69	34.86	969.00	40.19	963.74
0.7044	19.98	970.30	24.99	965.61	29.97	960.87	34.94	956.16	40.25	950.96
0.7981	19.99	961.08	24.99	956.19	30.05	951.41	34.86	946.87	40.18	941.78
0.9008	19.98	951.67	24.99	946.95	29.97	942.34	34.93	937.71	40.25	932.74
1.0000	19.98	944.07	25.03	939.39	29.97	934.85	34.94	930.27	40.26	925.43

× 10^{-5} in the most unfavorable case ($x_1 \approx 0.9$); for other concentrations, it was smaller. It should be noted, however, that there is also a systematic error in the concentrations resulting from the presence of H_2O in both the "pure" liquids. Actually, each investigated mixture is at least a ternary one (2-methylpyridine + D_2O + H_2O) with mole fractions of H_2O varying from 0.0036 to 0.0055 (the H_2O contents in 2-methylpyridine and in D_2O, respectively).

Ultrasonic Apparatus. The phase speed of ultrasound at 2.1 MHz was measured with a pulse−echo−overlap apparatus designed and constructed in our laboratory (electronic part) and at the Aeronautics Institute, Warsaw (ultrasonic cell). The sample cell was in the shape of a vertical cylinder approximately 30 mm in diameter with two transducers mounted on the side wall. The cell and the shields of the transducers were made of stainless steel 1H18N9T. A similar ultrasonic cup was described by Ernst et al. (1993). Water redistilled over $KMnO_4$ and NaOH, with an electrolytic conductivity of 1 × 10^{-4} S m^{-1}, was used for the calibration of the apparatus. The speeds of sound in H_2O, calculated from a polynomial given in the earlier work (Marczak, 1997b), were taken as true values. The temperature of the liquid sample was stabilized with a thermostat unit described previously (Ernst et al., 1996). Also the quartz thermometer mounted within the cell was the same as that used earlier (resolution of ±0.001 K). The speed of sound in the sample was calculated from the results of at least 10 consecutive measurements of the pulse repetition frequency. The scattering of the speed of sound values, resulting from the reproducibility of the pulse repetition measurements, is of the order of 1 cm s^{-1}; this value is very small in comparison with the attainable accuracy.

Although the precision of the speed of sound measurements was estimated to be approximately 0.01% (Zorębski et al., 1995), its accuracy is difficult to estimate because of the lack of reliable standard liquids. From the comparison of the experimental speeds of sound in 11 pure liquids with the data reported in various literature sources (Zorębski et al., 1995), it may be concluded that the accuracy is not worse than a few decimeters per second. Details concerning the velocimeter, a block diagram of the instrument, and the testing procedure were described by Zorębski et al. (1995).

Densimeter. A vibrating tube densimeter Unilab MG-2 was used for the density measurements with a precision of 5 × 10^{-2} kg m^{-3}. The accuracy is probably of the same order. It should be mentioned that, although vibrating tube instruments often provide a high sensitivity, achieving even 10^{-3} kg m^{-3}, it is very difficult to reach such a precision in a physicochemical laboratory. According to Kell (1977), for the measurement with a precision of 1 × 10^{-2} kg m^{-3} "...the density of laboratory water should be checked at one temperature and pressure against known standard (...), the uncertainty of the isotopic composition of the material to be measured is important also". Moreover, Bernhardt and Pauly (1980) found that the accuracy of the vibrating tube measurements is limited also by the viscosity differences between the sample and the standard liquid. This was confirmed by Ashcroft et al. (1990), according to whom the true density of a liquid of viscosity approximately 2 mPa s may be even 7 × 10^{-2} kg m^{-3} lower than that measured with a vibrating−tube apparatus calibrated with water ($\eta \approx 0.9$ mPa s). The following comment was given by Dr. S. J. Ashcroft in his review of this paper: "The effect of viscosity on density measurements is significant for high-

Table 4. Coefficients of the Speed of Ultrasound (u) Polynomials (1) for 2-Methylpyridine (1) + Heavy Water (2) for the Temperature Range (293−313) K with the Standard Deviations and Mean Deviations from the Regression Lines δ_u

x_1	u_0/(m s^{-1})	u_1/(m s^{-1} deg^{-1})	u_2/(m s^{-1} deg^{-2})	δ_u/(m s^{-1})
0.0000	1307.993 ± 0.324	4.4876 ± 0.0221	−0.033926 ± 0.000360	0.04
0.0200	1402.802 ± 0.227	2.6375 ± 0.0155	−0.025121 ± 0.000253	0.03
0.0404	1455.607 ± 0.420	1.4316 ± 0.0286	−0.020212 ± 0.000467	0.05
0.0484	1471.360 ± 0.490	1.0398 ± 0.0334	−0.018537 ± 0.000543	0.05
0.0593	1490.183 ± 0.508	0.5831 ± 0.0346	−0.017094 ± 0.000564	0.06
0.0776	1517.693 ± 0.695	−0.1306 ± 0.0473	−0.014270 ± 0.000770	0.08
0.0995	1544.080 ± 0.951	−0.8190 ± 0.0650	−0.012025 ± 0.001064	0.11
0.1858	1604.372 ± 0.451	−2.5435 ± 0.0307	−0.005118 ± 0.000502	0.05
0.2958	1622.495 ± 0.901	−3.3825 ± 0.0616	−0.003186 ± 0.001009	0.10
0.4062	1617.205 ± 0.075	−3.9396 ± 0.0024		0.04
0.5002	1597.419 ± 0.145	−4.0603 ± 0.0047		0.07
0.5923	1573.825 ± 0.450	−4.1864 ± 0.0307	0.001821 ± 0.000501	0.05
0.7044	1540.894 ± 0.503	−4.0871 ± 0.0344	0.000614 ± 0.000563	0.06
0.7981	1520.543 ± 0.513	−4.2317 ± 0.0350	0.003090 ± 0.000571	0.06
0.9008	1500.219 ± 0.727	−4.2218 ± 0.0496	0.002318 ± 0.000811	0.08
1.0000	1486.553 ± 0.376	−4.3584 ± 0.0257	0.003795 ± 0.000420	0.04

Table 5. Coefficients of the Density (ρ) Polynomials (1) for 2-Methylpyridine (1) + Heavy Water (2) for the Temperature Range (293−313) K with the Standard Deviations and Mean Deviations from the Regression Lines δ_ρ

x_1	ρ_0/(kg m^{-3})	ρ_1/(kg m^{-3} deg^{-1})	ρ_2/(kg m^{-3} deg^{-2})	δ_ρ/(kg m^{-3})
0.0000	1104.837 ± 0.450	0.1183 ± 0.0311	−0.006464 ± 0.000513	0.05
0.0200	1100.039 ± 0.559	−0.1290 ± 0.0387	−0.004766 ± 0.000641	0.06
0.0404	1094.251 ± 0.394	−0.2868 ± 0.0272	−0.003649 ± 0.000451	0.04
0.0484	1090.997 ± 0.584	−0.2809 ± 0.0404	−0.004059 ± 0.000668	0.06
0.0593	1087.465 ± 0.300	−0.2921 ± 0.0208	−0.004658 ± 0.000343	0.03
0.0776	1084.247 ± 0.430	−0.4807 ± 0.0298	−0.002550 ± 0.000490	0.05
0.0995	1078.379 ± 0.270	−0.5218 ± 0.0186	−0.002955 ± 0.000308	0.03
0.1858	1063.669 ± 0.080	−0.8797 ± 0.0026		0.04
0.2958	1042.750 ± 0.136	−0.8183 ± 0.0094	−0.002219 ± 0.000155	0.01
0.4062	1028.608 ± 0.252	−0.9806 ± 0.0174	−0.000365 ± 0.000288	0.03
0.5002	1012.963 ± 0.392	−0.8360 ± 0.0271	−0.002398 ± 0.000447	0.04
0.5923	1003.903 ± 0.476	−1.0258 ± 0.0329	0.000673 ± 0.000544	0.05
0.7044	988.357 ± 0.311	−0.8793 ± 0.0215	−0.001233 ± 0.000355	0.03
0.7981	980.092 ± 0.109	−0.9537 ± 0.0035		0.04
0.9008	970.292 ± 0.042	−0.9329 ± 0.0014		0.02
1.0000	962.807 ± 0.033	−0.9466 ± 0.0023	0.000450 ± 0.000038	0.00

precision density measurements but the magnitude of the effect is likely to be highly instrument-sensitive".

The apparatus used in the present study was checked using standard liquids (aqueous solutions of NaCl, $K_2Cr_2O_7$, and K_2CrO_4) whose densities were determined using bicapillary pycnometers described by Ernst et al. (1996). The differences in the measured densities did not exceed 7×10^{-2} kg m^{-3} (Brylska, 1992).

The densimeter was calibrated with air and redistilled water (the same as that used for the calibration of the ultrasonic apparatus) partially degassed by boiling before each measurement. The calibration procedure was repeated twice a day, before and after a series of measurements at a given temperature. It was assumed that the densities of water and air calculated from the equations given by Spieweck and Bettin (1993) are the true values. For the air density, the effects of temperature and atmospheric pressure were taken into account, while the relative humidity, which is of less importance, was supposed to be 50%. The tube oscillation frequencies were measured at least twice for each liquid. The fluctuations of the frequency imply an uncertainty in density of the order of 10^{-2} kg m^{-3}.

The temperature was measured with a Pt100 resistance thermometer (DRT-10, Sensor, resolution ±0.01 K).

Temperature Measurements and Scale. All temperatures reported in this work are expressed in the International Temperature Scale of 1990 (ITS-90). Where necessary, they were recalculated from the IPTS-68 values using a polynomial given by Blanke (Spieweck and Bettin, 1993).

The two thermometers mentioned earlier (the quartz oscillator used in the ultrasonic experiment and the Pt100 thermometer) were calibrated to comply with ITS-90. The Ertco-Hart Model 850 resistance thermometer (resolution ±0.001 K), equipped with a Pt100 probe Model 5613, was used as a reference device. Both the thermometer and the probe are certified to be traceable to NIST.

The accuracy of the temperature measurements with both the thermometers (the quartz one and the DRT-10 one) is of the order of ±0.05 K. This value is equal to the accuracy of the Ertco-Hart measuring set and is greater than the residual errors of the fit of the calibration curves of the quartz oscillator and the DRT-10.

It should be noted, however, that the discrepancies in densities and speeds of sound caused by the differences between the ITS-90 and IPTS-68 are very small in comparison to the measurement uncertainties.

Results

The speeds of sound and densities were measured at atmospheric pressure within the temperature range (293−313) K at approximately 5 K intervals and within the whole concentration range for 14 mixtures of 2-methylpyridine (1) with deuterium oxide (2), as well as for the pure components. The results are shown in Tables 2 and 3. For a given concentration the dependencies of the speed of sound (u) and density (ρ) on temperature could be satisfactorily approximated by parabolic ($n = 2$) or linear ($n = 1$) equations:

$$y = \sum_{i=0}^{n} a_i t^i \tag{1}$$

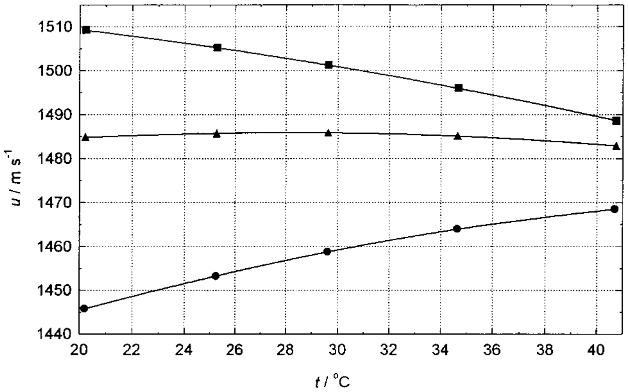

Figure 1. Speed of sound in the 2-methylpyridine (1) + heavy water (2) mixtures for the temperature range (293−313) K: (■) $x_1 = 0.0776$; (▲) $x_1 = 0.0484$; (●) $x_1 = 0.0200$; points, experimental values; lines, eq 1 with coefficients given in Table 4.

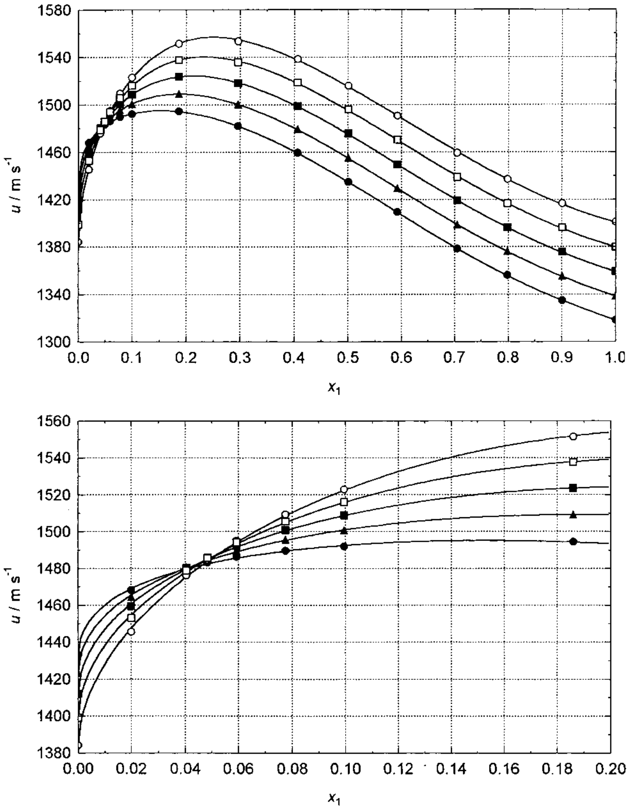

Figure 2. Speed of sound isotherms for 2-methylpyridine (1) + heavy water (2): (○) 293.15 K; (□) 298.15 K; (■) 303.15 K; (▲) 308.15 K; (●) 313.15 K; (top) in the whole concentration range; (bottom) in dilute solutions; points, values calculated from eq 1; lines, calculated from the empirical function: $u = \sum_{i=0}^{5} a_i x_1^i + a_6\sqrt{x_1} + a_7 \exp(x_1)$, where $a_2 = 0$.

where y is u or ρ, t is temperature in the centigrade scale (ITS-90), and a_i are constants. The a_i constants, calculated by the least-squares method, together with the mean deviations from the regression line, are collected in Tables 4 and 5 (where the coefficients $a_i = u_i$ for speed and $a_i = \rho_i$ for density, respectively), while examples of the $u = u(t)$ curves are plotted in Figure 1. As the criterion to choose between the linear and parabolic functions, the mean deviations from the regression lines were applied.

The adiabatic compressibility was calculated from the Laplace formula:

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

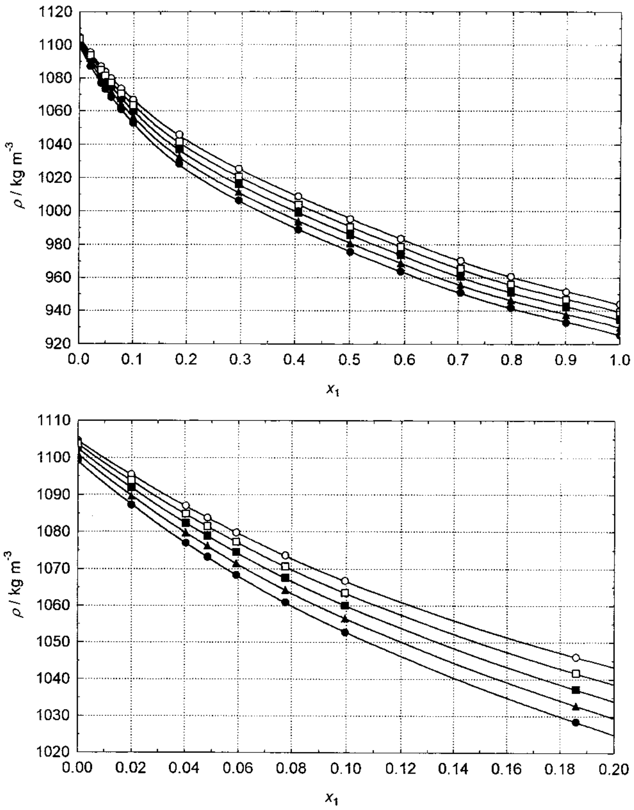

Figure 3. Density isotherms for 2-methylpyridine (1) + heavy water (2): symbols as in Figure 2; (top) in the whole concentration range; (bottom) in dilute solutions; points, values calculated from eq 1; lines, calculated from the empirical function $\rho = \sum_{i=0}^{5} a_i x_1^i$, where $a_i \neq 0$ (top) or $a_4 = a_5 = 0$ (bottom).

where ρ and u were calculated from eq 1. The density, speed of sound, and compressibility isotherms are plotted as functions of the mole fraction of 2-methylpyridine in Figures 2, 3, and 4, respectively.

Summary

The isotherms of density, speed of sound, and compressibility for 2-methylpyridine (1) + D_2O (2), given in Figures 2−4, are similar to those for 3-methylpyridine + D_2O (Marczak, 1996) although the phase properties of these systems are different (Schneider, 1973). In the temperature range studied, 2-methylpyridine is completely miscible with heavy water, while, for the system 3-methylpyridine + D_2O, a lower consolute point appears at 38.5 °C and at the mole fraction of amine $x \approx 0.077$ (Cox, 1952). Moreover, with increasing pressure, the two-phase region for the system containing 2-methylpyridine first vanishes and then, at $p \approx 2$ GPa, it appears again and increases afterward. For 3-methylpyridine + D_2O the loop merely shrinks but does not disappear, and it increases again at higher pressures (Schneider, 1973). The phase properties, however, seem to be not related to the features of the compressibility isotherms.

For both the systems the κ_S isotherms cross one another within a narrow concentration interval in the vicinity of $x \approx 0.04$. Similar crossing intervals were found for the mixtures of all three methylpyridine isomers with H_2O (Ernst and Marczak, 1992, 1995; Marczak and Ernst, 1998); those mixtures show no miscibility gap at atmospheric pressure. It is worthy of notice that, although the compressibilities of light and heavy water are different, the crossing points of the compressibility isotherms for their

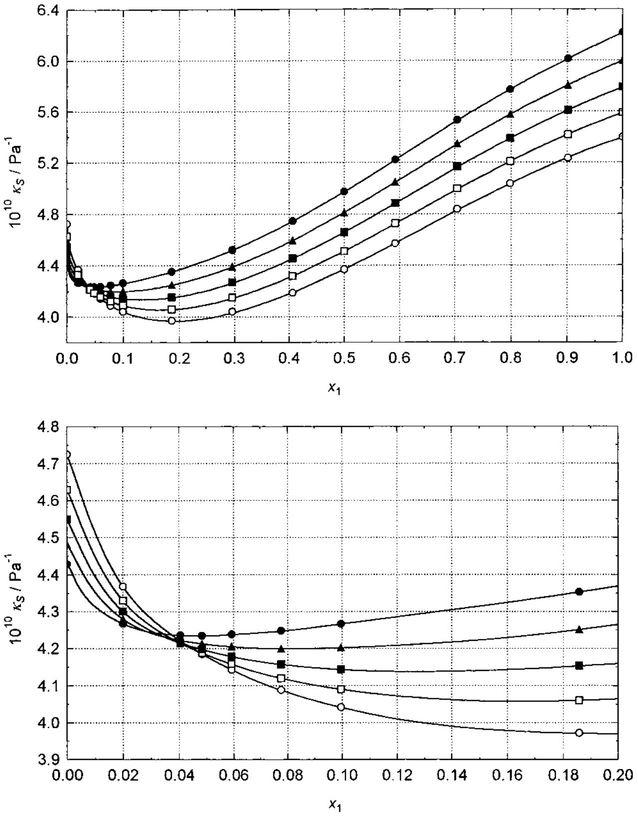

Figure 4. Adiabatic compressibility isotherms for 2-methylpyridine (1) + heavy water (2): symbols as in Figure 2; (top) in the whole concentration range; (bottom) in dilute solutions; lines, calculated from the empirical function $\kappa_S = \sum_{i=0}^{5} a_i x_1^i + a_6\sqrt{x_1} + a_7$ $\exp(x_1)$, where $a_2 = 0$ (top), or for cubic spline interpolation (bottom).

binary mixtures with 2- and 3-methylpyridine appear at nearly the same concentrations.

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