Speed of Ultrasound, Density, and Adiabatic Compressibility for 4-Methylpyridine + Heavy Water in the Temperature Range 293 K to 313 K

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The speed of ultrasound and density were measured for 4-methylpyridine (1) + heavy water (2) in the whole concentration range within the temperature interval (293 to 313) K. Second-order polynomials were used for the approximation of the speed and density dependencies on temperature at constant concentration. From the Laplace equation, the adiabatic compressibilities were calculated. The isotherms of the speed of sound and those of the compressibility have single extrema (maxima and minima, respectively), while the density decreases monotonically with increasing concentration of 4-methylpyridine. Within the mole fraction interval $x_1 \approx 0.03-0.06$, both the speed of sound and the compressibility isotherms cross each other. The isotherms for the investigated system are very similar to those for 3-methylpyridine + D_2O, but they differ quantitatively from those for 2-methylpyridine + D_2O discussed in previous papers.

Introduction

Water and its solutions have been investigated extensively in many laboratories. The main reason for that is the unique role of water in biological systems (e.g., Gutmann and Resch (1995)); however, because of the complexity of those systems, the investigation of simpler model systems seems to be more promising. For example, aqueous solutions of amphipathic substances can be used as those model systems.

The effects of intermolecular interactions are revealed in the thermodynamic properties of solutions. Therefore, classical thermodynamics can be applied to the investigation of the molecular order in solutions, although the thermodynamic approach neglects the molecular structure of matter. Since molecular acoustics is, in contrast to thermodynamics, a molecular theory, the speed of sound in a liquid can be expressed in terms of its molecular structure. The agreement of speeds of sound predicted theoretically with experimental data is, however, attainable only for binary mixtures of components with relatively simple molecules (see Sivakumar et al. (1986) for a comparison of the applications of the free length theory, the collision factor theory, and Kudryavtsev's theory used for that purpose). For aqueous solutions, the thermodynamic approach is rather preferred, the speeds of sound being applied in the calculation of the adiabatic compressibility. The dependence of that quantity on temperature and concentration can be explained using various molecular models (e.g., Endo (1973), Ernst and Glinski (1977), Jerie et al. (1983), and Ernst and Marczak (1992)). Alternatively, ternary mixtures can be investigated (Antosiewicz et al., 1987) or the properties of binary aqueous solutions can be compared with those of deuterium oxide (Miyai et al., 1997).

This work deals with the mixtures 4-methylpyridine (1) + heavy water (2). The speeds of ultrasound, densities, and adiabatic compressibilities for 2- and 3-methylpyridine + D_2O and for 4-methylpyridine + H_2O have been reported earlier (Marczak, 1996, 1999; Ernst and Marczak, 1992). In the latter paper, the dependencies of the compressibility and molar volume of aqueous 4-methylpyridine solutions on temperature and concentration were discussed in terms of hydrophobic and hydrophilic hydration. As indicated by the enthalpies of mixing (Marczak and Giera, 1998), there are small, but significant, differences between the properties of dilute solutions of the methylpyridine isomers in light water and those in heavy water. Therefore, measurements of the speed of sound and density of the methylpyridine + D_2O mixtures have been undertaken to obtain data that are complementary to those reported earlier for the 2-, 3-, and 4-methylpyridine + H_2O binaries (Ernst and Marczak, 1992, 1995; Marczak and Ernst, 1998).

Table 1. Density ρ and Refractive Index n_D of 4-Methylpyridine at $T = 298.15$ K and the Mole Fraction of Water x As Determined by the Karl Fischer Method

	exptl	lit.
$\rho/(\text{kg m}^{-3})$	949.63 ± 0.05	950.1[a]
n_D	1.5025 ± 0.0002	1.5030[b]
$100x$	0.23 ± 0.01	

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

Experimental Section

Chemicals. 4-Methylpyridine (Aldrich, 98% by mass) was distilled in a rectifying column under atmospheric pressure. Its density, refractive index, and the concentration of water, determined by the Karl Fischer titration, are given in Table 1. The differences between the experimental data and those reported in the literature are most probably due to the various contents of water and 2-methylpyridine which contaminates commonly 4-methylpyridine.

The heavy water (from Sigma) used in this experiment was the same as that one used in the previous work. Its isotopic purity, estimated from the speed of sound and density data, was 99.45 and 99.35 mol %, respectively (Marczak, 1999).

The solutions were prepared by mass using an analytical balance and stored in sealed flasks. The corrections for

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Table 2. Speeds of Ultrasound (u) in 4-Methylpyridine (1) + Heavy Water (2) Measured with a 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[a]	20.19	1384.78	25.22	1399.56	29.59	1411.07	34.63	1422.74	40.66	1434.36
0.0204	20.19	1439.63	25.24	1447.28	29.61	1452.94	34.62	1458.22	40.65	1462.85
0.0397	20.19	1462.31	25.24	1465.71	29.61	1467.83	34.62	1469.25	40.66	1469.46
0.0473	20.21	1469.44	25.24	1471.35	29.62	1472.26	34.65	1472.36	40.71	1471.03
0.0587	20.23	1478.43	25.26	1478.34	29.62	1477.64	34.67	1475.94	40.74	1472.58
0.0776	20.23	1491.42	25.26	1488.47	29.63	1485.39	34.67	1481.08	40.74	1474.73
0.1004	20.20	1504.31	25.20	1498.47	29.50	1493.14	34.49	1486.22	40.52	1476.93
0.1853	20.23	1534.91	25.26	1521.91	29.62	1510.54	34.65	1497.22	40.72	1480.72
0.2999	20.19	1545.16	25.16	1528.02	29.49	1513.23	34.49	1496.10	40.53	1475.08
0.3944	20.21	1539.07	25.24	1519.91	29.57	1503.55	34.54	1484.85	40.57	1462.07
0.4925	20.23	1524.63	25.25	1504.71	29.63	1487.53	34.66	1467.82	40.76	1444.11
0.5993	20.20	1505.30	25.22	1485.04	29.58	1467.66	34.60	1447.78	40.63	1423.96
0.6980	20.18	1486.84	25.20	1466.56	29.54	1449.20	34.55	1429.24	40.58	1405.26
0.8046	20.20	1469.47	25.22	1449.05	29.59	1431.54	34.61	1411.61	40.67	1387.62
0.8958	20.19	1456.29	25.20	1435.69	29.57	1418.00	34.57	1397.93	40.60	1373.83
1.0000	20.19	1444.81	25.19	1423.97	29.49	1406.29	34.47	1386.04	40.49	1361.75

[a] The data for pure deuterium oxide are the same as those reported earlier (Marczak, 1999) and are given here for the reader's convenience.

Table 3. Densities (ρ) of 4-Methylpyridine (1) + Heavy Water (2) Measured with a 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[a]	19.98	1104.60	25.03	1103.80	29.97	1102.53	34.95	1101.08	40.27	1099.12
0.0204	19.99	1094.35	24.99	1092.95	30.06	1090.96	34.86	1088.93	40.17	1086.24
0.0397	19.99	1085.60	24.99	1083.38	30.05	1080.99	34.85	1078.62	40.18	1075.44
0.0473	19.97	1082.08	24.98	1079.88	29.97	1077.45	35.06	1074.57	40.20	1071.51
0.0587	19.96	1077.64	24.98	1075.08	29.97	1072.38	35.06	1069.30	40.20	1066.19
0.0776	19.96	1070.66	25.03	1067.67	30.07	1064.53	35.11	1061.37	40.15	1058.00
0.1004	19.93	1063.11	24.99	1059.87	29.97	1056.61	34.99	1053.12	40.25	1049.25
0.1853	19.96	1041.58	25.03	1037.42	30.07	1033.22	35.11	1029.04	40.16	1024.71
0.2999	19.93	1021.32	24.99	1016.88	29.97	1012.42	34.99	1007.73	40.25	1002.65
0.3944	19.98	1007.77	24.97	1003.07	30.06	998.18	34.86	993.59	40.17	988.07
0.4925	19.93	995.88	25.03	991.12	30.07	986.27	35.11	981.39	40.16	976.46
0.5993	19.98	984.73	24.97	980.04	30.06	975.22	34.86	970.64	40.18	965.34
0.6980	19.93	975.40	24.99	970.80	29.97	966.22	35.00	961.54	40.25	956.57
0.8046	19.98	967.09	24.97	962.56	30.06	957.84	34.86	953.37	40.17	948.18
0.8958	19.93	960.54	24.99	955.75	29.97	951.23	34.99	946.68	40.25	941.80
1.0000	19.98	954.12	25.03	949.58	29.97	945.17	34.99	940.58	40.25	935.75

[a] The data for pure deuterium oxide are the same as those reported earlier (Marczak, 1999) and are given here for the reader's convenience.

Table 4. Coefficients of the Speed of Ultrasound (u) Polynomials (1) for 4-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[a]	1307.993 ± 0.324	4.4876 ± 0.0221	−0.033 926 ± 0.000 360	0.04
0.0204	1395.971 ± 0.270	2.6708 ± 0.0184	−0.025 223 ± 0.000 301	0.03
0.0397	1437.554 ± 0.275	1.6595 ± 0.0187	−0.021 510 ± 0.000 306	0.03
0.0473	1451.317 ± 0.379	1.3015 ± 0.0258	−0.020 065 ± 0.000 421	0.04
0.0587	1469.259 ± 0.406	0.8173 ± 0.0276	−0.018 050 ± 0.000 450	0.05
0.0776	1495.007 ± 0.476	0.1353 ± 0.0324	−0.015 525 ± 0.000 527	0.05
0.1004	1520.628 ± 0.649	−0.5435 ± 0.0443	−0.013 191 ± 0.000 724	0.07
0.1853	1584.634 ± 0.422	−2.3675 ± 0.0287	−0.004 516 ± 0.000 468	0.05
0.2999	1613.472 ± 0.848	−3.3585 ± 0.0579	−0.001 356 ± 0.000 947	0.09
0.3944	1616.237 ± 0.501	−3.8387 ± 0.0341	0.000 970 ± 0.000 558	0.06
0.4925	1605.816 ± 0.197	−4.0600 ± 0.0134	0.002 270 ± 0.000 219	0.02
0.5993	1587.838 ± 0.475	−4.1417 ± 0.0324	0.002 664 ± 0.000 529	0.05
0.6980	1569.157 ± 0.453	−4.1197 ± 0.0309	0.002 003 ± 0.000 505	0.05
0.8046	1552.908 ± 0.534	−4.2001 ± 0.0364	0.003 351 ± 0.000 594	0.06
0.8958	1540.853 ± 0.585	−4.2657 ± 0.0399	0.003 757 ± 0.000 652	0.06
1.0000	1530.977 ± 0.420	−4.3581 ± 0.0287	0.004 428 ± 0.000 469	0.05

[a] The polynomial coefficients for pure deuterium oxide are the same as those reported earlier (Marczak, 1999) and are given here for the reader's convenience.

weighing in air were neglected because the densities of the mixture components are close to one another. Although the random error in the mole fraction estimated from the balance accuracy was 5 × 10^{-5} in the most unfavorable case ($x_1 \approx 0.9$), the systematic error in the concentrations is much greater. Because H_2O is present in both "pure" liquids, each solution is contaminated by H_2O; its mole fraction varies from 0.0023 to 0.0055 (the H_2O contents in 4-methylpyridine and in D_2O, respectively).

Apparatus. The measuring sets and calibration procedures were described in the earlier paper (Marczak, 1999). The phase speed of the ultrasound of 2.1 MHz frequency was measured by a pulse-echo-overlap apparatus designed and constructed in our laboratory (electronic part) and at

Table 5. Coefficients of the Density (ρ) Polynomials (1) for 4-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[a]	1104.837 ± 0.450	0.1183 ± 0.0311	−0.006 464 ± 0.000 513	0.05
0.0204	1097.073 ± 0.061	0	−0.006 712 ± 0.000 058	0.06
0.0397	1091.672 ± 0.852	−0.2091 ± 0.0589	−0.004 824 ± 0.000 975	0.09
0.0473	1088.083 ± 0.383	−0.1894 ± 0.0265	−0.005 557 ± 0.000 438	0.04
0.0587	1086.146 ± 0.496	−0.3547 ± 0.0343	−0.003 537 ± 0.000 567	0.05
0.0776	1081.359 ± 0.299	−0.4905 ± 0.0207	−0.002 270 ± 0.000 343	0.03
0.1004	1074.007 ± 0.261	−0.4817 ± 0.0181	−0.003 307 ± 0.000 299	0.03
0.1853	1057.443 ± 0.298	−0.7753 ± 0.0207	−0.000 982 ± 0.000 342	0.03
0.2999	1037.135 ± 0.150	−0.7326 ± 0.0104	−0.003 081 ± 0.000 172	0.02
0.3944	1024.967 ± 0.814	−0.8066 ± 0.0563	−0.002 762 ± 0.000 932	0.09
0.4925	1013.991 ± 0.236	−0.8822 ± 0.0163	−0.001 309 ± 0.000 270	0.03
0.5993	1002.469 ± 0.418	−0.8538 ± 0.0289	−0.001 737 ± 0.000 478	0.05
0.6980	992.858 ± 0.074	−0.8513 ± 0.0051	−0.001 246 ± 0.000 084	0.01
0.8046	984.104 ± 0.384	−0.8108 ± 0.0266	−0.002 068 ± 0.000 439	0.04
0.8958	978.797 ± 0.118	−0.9191 ± 0.0038	0	0.06
1.0000	971.525 ± 0.188	−0.8539 ± 0.0130	−0.000 870 ± 0.000 215	0.02

[a] The polynomial coefficients for pure deuterium oxide are the same as those reported earlier (Marczak, 1999) and are given here for the reader's convenience.

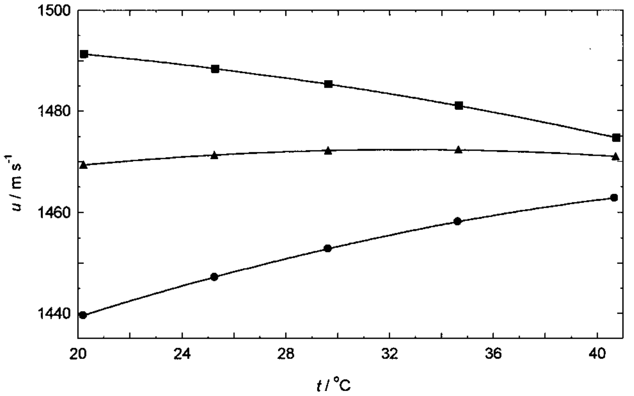

Figure 1. Speed of sound in the 4-methylpyridine (1) + heavy water (2) mixtures for the temperature range 293 K to 313 K: (■) $x_1 = 0.0776$; (▲) $x_1 = 0.0473$; (●) $x_1 = 0.0204$; (points) experimental values; (lines) eq 1 with coefficients given in Table 4.

the Aeronautics Institute, Warsaw (ultrasonic cell). The details were given by Zorebski et al. (1995). The density was determined with a vibrating-tube densimeter Unilab MG-2. Both of the instruments were calibrated using as standard liquid water redistilled over $KMnO_4$ and NaOH with an electrolytic conductivity of 1×10^{-4} S m^{-1}. The precisions of the speed of sound and density measurements were estimated to be 0.1 m s^{-1} and 0.05 kg m^{-3}, respectively. The latter value seems to be close to the accuracy, while the accuracy of speed of sound measurements is rather difficult to declare due to the lack of reliable standards. It is probably of the order of a few decimeters per second.

The thermometers used in this experiment (a quartz thermometer mounted in the ultrasonic cell and a platinum resistance one in the densimeter) were calibrated to comply with the International Temperature Scale of 1990 (ITS-90). Their accuracy was estimated to be ±0.05 K, while the resolutions were much better: 0.001 K for the quartz thermometer and 0.01 K for the resistance one. The discrepancies in speeds and densities caused by the difference between ITS-90 and IPTS-68 are small in comparison with the measurement accuracy. The details were described in the previous work (Marczak, 1999).

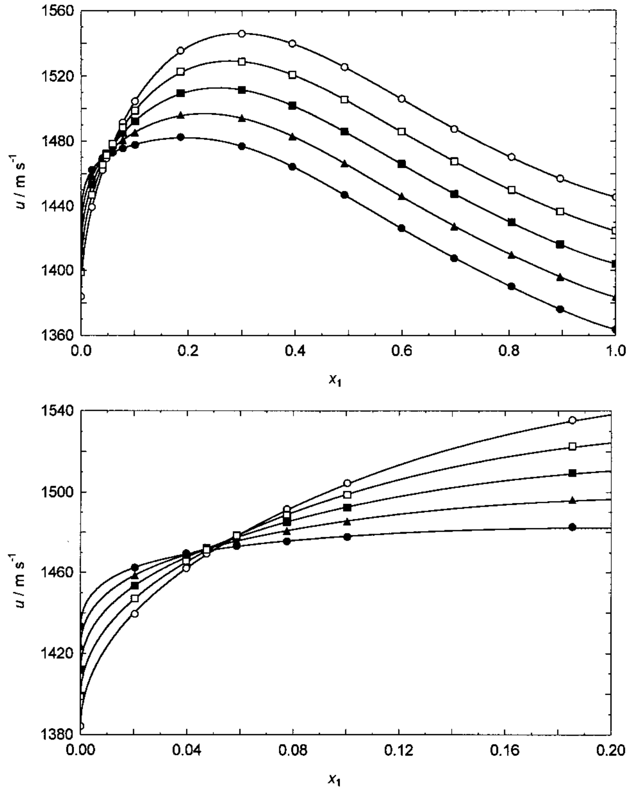

Figure 2. Speed of sound isotherms for 4-methylpyridine (1) + heavy water (2) in the whole concentration range (top) and in dilute solutions (bottom): (○) 293.15 K; (□) 298.15 K; (■) 303.15 K; (▲) 308.15 K; (●) 313.15 K; (points) values calculated from eq 1; (lines) calculated from the empirical function: $u = \sum_{i=0}^{5} a_i x_1^i + a_6 x_1^{1/2} + a_7 \exp(x_1)$.

Results

The speeds of ultrasound and the densities were measured for the 4-methylpyridine (1) + heavy water (2) system in the whole composition range at temperatures ranging from 293 to 313 K. The data obtained from the measurements are given in Tables 2 and 3. Both the temperature dependencies of the speed (u) and density (ρ) at a given concentration may be approximated by the following second-order polynomial:

$$y = \sum_{i=0}^{2} a_i t^i \qquad (1)$$

where y is u or ρ, t is the temperature in degrees centigrade, and a_i are constants; their values, calculated by the least-

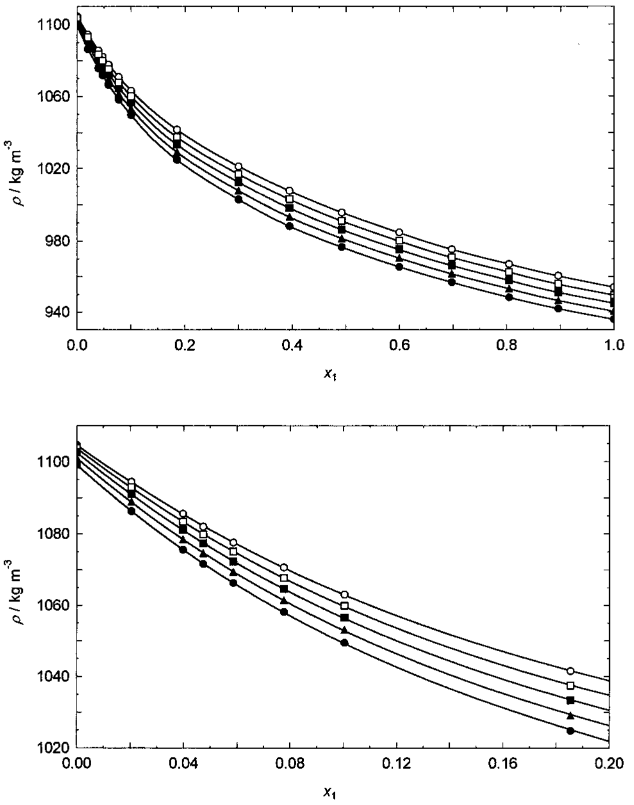

Figure 3. Density isotherms for 4-methylpyridine (1) + heavy water (2) in the whole concentration range (top) and in dilute solutions (bottom): symbols as in Figure 2; (points) values calculated from eq 1; (lines) calculated by the cubic spline procedure (top) or from the empirical function $\rho = \sum_{i=0}^{3} a_i x_1^{\,i}$ (bottom).

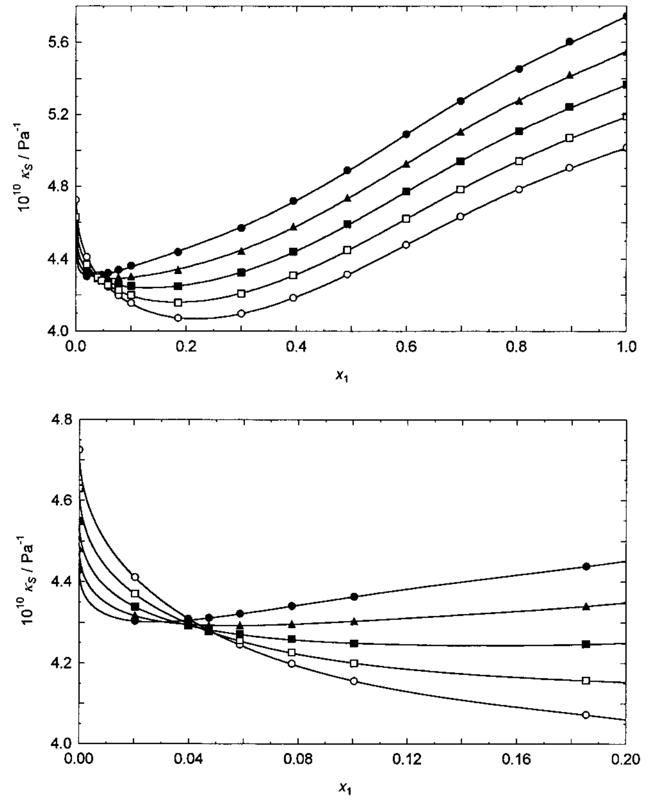

Figure 4. Adiabatic compressibility isotherms for 4-methylpyridine (1) + heavy water (2) in the whole concentration range (top) and in dilute solutions (bottom): symbols as in Figure 2; (points) values calculated from the Laplace formula (eq 2); (lines) calculated from the empirical function $\kappa_s = \sum_{i=0}^{5} a_i x_1^{\,i} + a_6 x_1^{1/2} + a_7 \exp(x_1)$, where $a_i \neq 0$ (top) or $a_2 = a_3 = a_5 = 0$ (bottom).

squares method, are collected in Tables 4 and 5 (where $a_i = u_i$ for speed and $a_i = \rho_i$ for density, respectively). As indicated by the results of the *F*-testing, some of the regression coefficients in the density functions are equal to zero. Examples of the $u = u(t)$ functions are plotted in Figure 1. The speed of sound and density values, calculated from eq 1 for the temperature interval 293.15 K to 313.15 K with a 5 K step, were plotted in Figures 2 and 3, respectively.

To determine the adiabatic compressibility coefficient, κ_S, the speeds of ultrasound and densities calculated from eq 1 were used in the Laplace formula:

$$\kappa_S = 1/(\rho u^2) \tag{2}$$

The compressibility isotherms are drawn in Figure 4.

Summary

The speed of ultrasound and adiabatic compressibility isotherms show two points of interest: a narrow crossing interval at low 4-methylpyridine mole fractions ($x_1 = 0.05 \pm 0.01$ and $x_1 = 0.04 \pm 0.01$, respectively) and extrema, in the x_1 ranges 0.2−0.3 and 0.02−0.25, respectively. Both the crossing points of the isotherms and extrema are shifted toward smaller 4-methylpyridine concentrations with increasing temperature (Figures 2 and 4). The density decreases monotonically when x_1 increases (Figure 3).

The isotherms presented here are very similar to those of the 3-methylpyridine + D_2O system (Marczak, 1996). The properties of both systems, 3-methylpyridine + D_2O and 4-methylpyridine + D_2O, differ quantitatively from those of the 2-methylpyridine + D_2O one (Marczak, 1999), but the major features of the isotherms of the speed of ultrasound, density, and compresssibility are similar for all three mixtures. In an earlier work (Marczak and Giera, 1998), similarities and differences in the excess molar and partial enthalpies for those systems have been reported. Also, some concepts concerning the molecular order in the mixtures of the methylpyridine isomers with light and heavy water have been suggested.

The features of the adiabatic compressibility isotherms for the binary mixtures of methylpyridine with H_2O were discussed earlier (Ernst and Marczak, 1992, 1995; Marczak and Ernst, 1998). They led to the conclusion that in dilute aqueous solutions the hydrophobic hydration determines predominantly the mixture properties. It was suggested that at the mole fraction of methylpyridine slightly smaller than 0.05, there arises probably a clathrate-like structure similar to the solid hydrate of type II (Jeffrey and McMullan, 1967). The unit cell of that structure contains 136 hydrogen-bonded water molecules and 8 large hexacaidehedral voids in which single methylpyridine molecules may be accommodated. This structure is probably relatively temperature-resistant; thus, the adiabatic compressibility of the solution with the methylpyridine mole fraction close to 0.05 is almost independent of temperature; and consequently the κ_S isotherms cross each other at that concentration. At higher concentrations, the shortage of water diminishes the likelihood of the formation of an undisturbed hydration shell around the nonpolar moiety of the methylpyridine molecule and the hydrophilic interactions of either dipole−dipole or hydrogen-bond N···H−O type become more pronounced. A detailed discussion and a comparison of the six binaries methylpyridine isomer + (H_2O or D_2O) will be given in a next work.

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