

Table III. Sources of Solubility Data for Ammonia for Determination of Hydrogen-Bonding Factors

butanol	C <sub>4</sub> H <sub>10</sub> , C <sub>3</sub> H <sub>8</sub> (7); C <sub>2</sub> H <sub>6</sub> , CH <sub>4</sub> (18), C <sub>2</sub> H <sub>4</sub> (19); O <sub>2</sub> (20); C <sub>2</sub> H <sub>2</sub> (12); H <sub>2</sub> S, NH <sub>3</sub> , this work
ethanol	C <sub>4</sub> H <sub>10</sub> , C <sub>3</sub> H <sub>8</sub> , CH <sub>4</sub> , C <sub>2</sub> H <sub>4</sub> , CO <sub>2</sub> , N <sub>2</sub> O, He, NH <sub>3</sub> (2); C <sub>2</sub> H <sub>6</sub> (18); O <sub>2</sub> (20)
ethylene glycol	C <sub>2</sub> H <sub>6</sub> (21); C <sub>2</sub> H <sub>4</sub> (19); C <sub>2</sub> H <sub>2</sub> (12); CO <sub>2</sub> (22); H <sub>2</sub> S, NH <sub>3</sub> , this work
methanol	C <sub>4</sub> H <sub>10</sub> , C <sub>3</sub> H <sub>8</sub> , C <sub>2</sub> H <sub>4</sub> , CH <sub>4</sub> , SO <sub>2</sub> , He, N <sub>2</sub> O, NH <sub>3</sub> , CO <sub>2</sub> (2); C <sub>2</sub> H <sub>6</sub> (18); C <sub>2</sub> H <sub>2</sub> (12); O <sub>2</sub> (20); H <sub>2</sub> S, this work

related to those in another polar solvent.

In Figure 3 hydrogen-bonding factors for various gases in ethanol, butanol, and ethylene glycol are shown as a function of the hydrogen-bonding factor in methanol. It is evident that there is a close relation between the hydrogen-bonding factors in one of the alcohols and those of the other alcohol solvents. Although it is difficult to predict solubilities accurately from graphs such as that shown in Figure 3, the relation is at least semiquantitative. For all four solvents it would appear that some degree of chemical reaction occurs with ammonia, yielding hydrogen-bonding factors in excess of 1. On the other hand, the hydrogen-bonding factors for hydrogen sulfide in three of the alcohols are less than 1 and are generally consistent with the hydrogen-bonding factors for the other gases for which solubilities are available. Data for the hydrogen-bonding factors shown in Figure 3 are from sources given in Table III.

#### Glossary

$L$	Ostwald coefficient, cm <sup>3</sup> of gas (cm <sup>3</sup> of solvent) <sup>-1</sup>
$m$	volume of dry gas absorbed, cm <sup>3</sup>
$p_1$	partial pressure of gas, kPa
$p$	total pressure, kPa
$p_1^{\circ}$	vapor pressure of pure liquified gas, kPa
$p_2^{\circ}$	vapor pressure of pure solvent, kPa
$r$	solvent injection rate, cm <sup>3</sup> s <sup>-1</sup>
$R$	gas constant
$T$	absolute temperature, K
$V_1$	molar volume of gas at 101.325-kPa pressure, m <sup>3</sup> mol <sup>-1</sup>

$V_2$	molar volume of solvent, m <sup>3</sup> mol <sup>-1</sup>
$x_1$	mole fraction gas solubility at a gas partial pressure of 101.325 kPa
$x_1^i$	ideal gas solubility defined by eq 2
$Z$	gas compressibility factor
$\alpha$	hydrogen-bonding factor defined by eq 1
$\theta$	elapsed time for solubility measurement, s

**Registry No.** Acetone, 67-64-1; butanol, 71-36-3; chlorobenzene, 108-90-7; ethylene glycol, 107-21-1; methanol, 67-56-1; tetrahydrofuran, 109-99-9; acetic acid, 64-19-7; ammonia, 7664-41-7; hydrogen sulfide, 7783-06-4.

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Received for review May 14, 1982. Accepted October 19, 1982. We acknowledge with thanks an operating grant from the National Science and Engineering Research Council of Canada in support of this research.

## Ultrasonic Speeds and Isentropic Compressibilities for Binary Mixtures of 1-Hexanol with Hexane Isomers at 298.15 K<sup>†</sup>

Mavinkal K. Kumaran,<sup>‡</sup> George C. Benson,\* and Carl J. Halpin

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

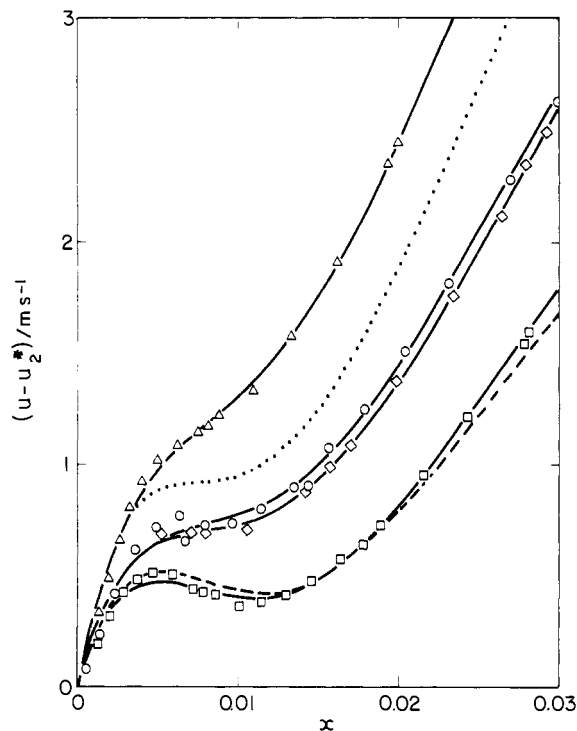
**The effect of isomeric variations of one of the components of a binary mixture on its thermodynamic properties was studied by measuring ultrasonic speeds for mixtures of 1-hexanol with the four isomers of *n*-hexane. Isentropic compressibilities were calculated from the results by using excess volumes reported previously.**

An earlier study (1) of binary mixtures of 1-hexanol with *n*-alkanes showed that the speed of sound and the excess

isentropic compressibility varied regularly as the number of carbon atoms in the hydrocarbon increased from 5 to 10. Moreover, the behavior of these properties in the region of high dilution of 1-hexanol was characterized by the appearance of unusual extrema or points of inflection for all of the mixtures. In order to investigate the effect of changes in the molecular configuration of the hydrocarbon, we have measured the speed of ultrasound in binary mixtures of 1-hexanol with the four isomers of *n*-hexane: 2-methylpentane (2-MP), 3-methylpentane (3-MP), 2,2-dimethylbutane (2,2-DMB), and 2,3-dimethylbutane (2,3-DMB). A priori, the results for these systems were expected to fall between those for mixtures of 1-hexanol with *n*-pentane and with *n*-hexane.

<sup>†</sup> Issued as NRCC No. 20782.

<sup>‡</sup> National Research Council of Canada Research Associate.



**Figure 1.** Deviations of ultrasonic speed,  $u$ , for 1-hexanol-hexane isomer mixtures at 298.15 K from the speed  $u_2^*$  for the hexane isomer, plotted for low mole fractions,  $x$ , of 1-hexanol. Points: (O) 2-MP; (□) 3-MP; (Δ) 2,2-DMB; (◇) 2,3-DMB. Curves for n-C6 (---) and n-C5 (···) are taken from ref 1.

### Experimental Section

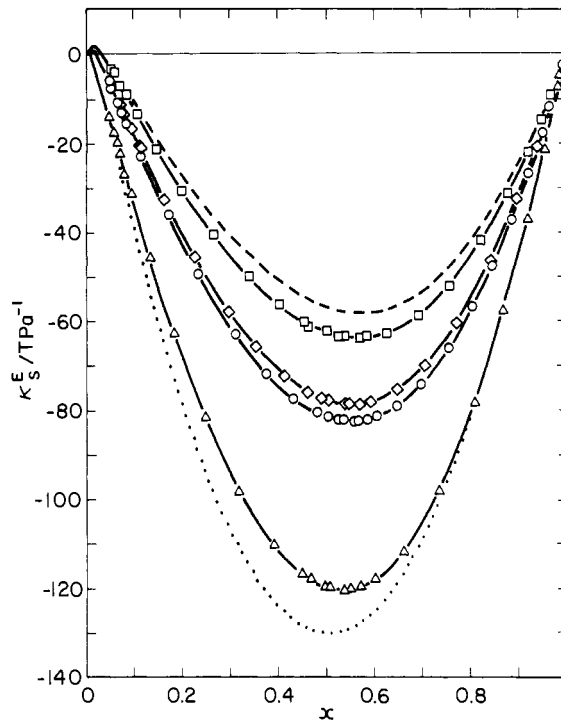
Practical-grade 1-hexanol (95 mol %) from Matheson Coleman and Bell was purified by preparative gas chromatography using a 4-m column containing 20 mass % Apiezon L on Chromosorb W (40/60 mesh). The density of the sample at 298.15 K was  $815.28 \text{ kg m}^{-3}$ . Research-grade isomeric hexanes from Phillips Petroleum Co. were used without further purification. The densities of these materials were reported previously (2).

The ultrasonic speeds for 2-MHz waves were determined at 298.15 K by a pulse-echo-overlap technique in a successive dilution cell. Experimental details can be found in previous publications (3, 4). Calibration of the cell was based on a value of  $1496.739 \text{ m s}^{-1}$  for the speed of ultrasound in water at 298.15 K (5). The error of the relative ultrasonic speeds is estimated to be less than  $0.2 \text{ m s}^{-1}$ , and their reproducibility was about  $0.02 \text{ m s}^{-1}$ . The error of the mole fractions is less than  $1 \times 10^{-4}$ .

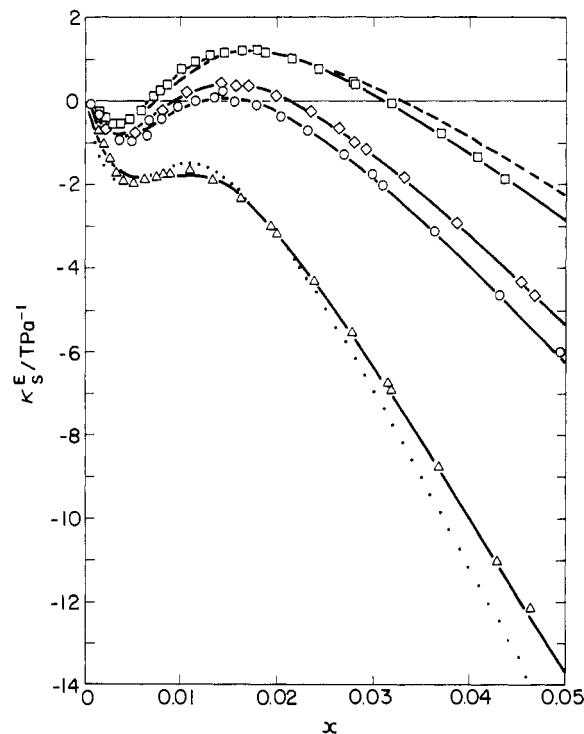
### Results and Discussion

The experimental values of the speed of sound,  $u$ , for the four binary mixtures are listed in Table I. In all cases,  $x$  is the mole fraction of 1-hexanol. Also given in Table I are values of the isentropic compressibility,  $\kappa_S$ , and of the excess isentropic compressibility,  $\kappa_S^E$ , calculated by the method outlined in an earlier paper (1). Densities of the mixtures were estimated from the densities of the components and the molar excess volumes (2). The values of the molar isobaric heat capacities,  $C_p^*$ , and isobaric thermal expansivities,  $\alpha_p^*$ , used in the calculations are summarized in Table II along with their sources (6, 7).

A plot of  $u$  against  $x$  (not shown) is similar to that reported previously (1) for 1-hexanol- $n$ -alkane mixtures. For the most part, the curves for the present mixtures fall between those for  $n$ -pentane (n-C5) and  $n$ -hexane (n-C6) with only the curve for 2,2-DMB falling a little outside this range. The results at high



**Figure 2.** Excess isentropic compressibilities,  $\kappa_S^E$ , of 1-hexanol-hexane isomer mixtures at mole fraction,  $x$ , of 1-hexanol and 298.15 K: (O) 2-MP; (□) 3-MP; (Δ) 2,2-DMB; (◇) 2,3-DMB. Curves are least-squares representations of our results by eq 1; curves for n-C6 (---) and n-C5 (···) are taken from ref 1.



**Figure 3.** Excess isentropic compressibilities,  $\kappa_S^E$ , of 1-hexanol-hexane isomer mixtures at low mole fractions,  $x$ , of 1-hexanol and 298.15 K: (O) 2-MP; (□) 3-MP; (Δ) 2,2-DMB; (◇) 2,3-DMB. Curves are least-squares representations of our results by eq 1 and 2; curves for n-C6 (---) and n-C5 (···) are taken from ref 1.

dilutions of 1-hexanol are shown in Figure 1, where deviations of the ultrasonic speed from the speed  $u_2^*$  for the pure alkane are plotted for  $x < 0.05$ . The behavior in this region closely parallels that found for the  $n$ -alkanes (1).

As in the case of 1-hexanol- $n$ -alkane mixtures, no smoothing function could be found which satisfactorily fitted the excess

Table I. Speed of Sound,  $u$ , Isentropic Compressibility,  $\kappa_S$ , and Excess Isentropic Compressibility,  $\kappa_S^E$ , for 1-Hexanol-Hexane Isomer Mixtures at Mole Fraction  $x$  of 1-Hexanol and 298.15 K

$x$	$u/(m\ s^{-1})$	$\kappa_S/TPa^{-1}$	$\kappa_S^E/TPa^{-1}$	$x$	$u/(m\ s^{-1})$	$\kappa_S/TPa^{-1}$	$\kappa_S^E/TPa^{-1}$
1-Hexanol-2-Methylpentane							
0.000 00	1040.86	1423.28	0.00	0.116 45	1058.29	1338.01	-22.78
0.000 60	1040.94	1422.88	-0.09	0.173 79	1069.40	1292.02	-35.96
0.001 44	1041.09	1422.20	-0.34	0.235 27	1082.59	1242.02	-49.34
0.002 45	1041.29	1421.36	-0.66	0.312 72	1100.29	1180.17	-62.97
0.003 61	1041.47	1420.49	-0.94	0.377 85	1116.25	1129.03	-71.82
0.004 91	1041.58	1419.78	-0.98	0.433 00	1130.59	1086.36	-77.46
0.006 38	1041.63	1419.17	-0.83	0.479 27	1143.10	1051.30	-80.61
0.006 70	1041.51	1419.37	-0.47	0.503 90	1149.80	1033.17	-81.44
0.007 92	1041.58	1418.78	-0.43	0.525 84	1156.17	1016.66	-82.36
0.009 64	1041.59	1418.18	-0.14	0.534 31	1158.43	1010.72	-82.24
0.011 49	1041.66	1417.37	0.00	0.558 01	1165.45	993.19	-82.68
0.013 48	1041.76	1416.43	0.09	0.566 40	1167.74	987.40	-82.36
0.014 33	1041.76	1416.13	0.24	0.586 28	1173.73	972.95	-82.27
0.015 60	1041.93	1415.22	-0.02	0.604 36	1178.91	960.47	-81.40
0.017 87	1042.11	1413.96	-0.10	0.646 83	1191.75	930.96	-79.12
0.020 37	1042.37	1412.39	-0.37	0.698 51	1207.59	896.35	-74.22
0.023 15	1042.68	1410.59	-0.72	0.756 16	1225.61	859.30	-66.15
0.026 95	1043.14	1408.03	-1.30	0.806 49	1241.45	828.49	-56.68
0.029 91	1043.51	1406.00	-1.77	0.847 12	1254.30	804.63	-47.43
0.030 86	1043.67	1405.24	-2.03	0.886 73	1266.88	782.20	-37.07
0.036 30	1044.44	1401.28	-3.13	0.922 05	1278.10	762.92	-26.70
0.043 14	1045.47	1396.14	-4.65	0.950 93	1287.27	747.63	-17.44
0.049 34	1046.41	1391.50	-5.99	0.970 07	1293.35	737.74	-10.92
0.054 85	1047.35	1387.11	-7.44	0.984 80	1297.97	730.31	-5.65
0.067 68	1049.54	1376.94	-10.71	0.993 16	1300.58	726.16	-2.57
0.077 27	1051.17	1369.41	-13.03	1.000 00	1302.72	722.78	0.00
0.086 28	1052.77	1362.19	-15.32				
1-Hexanol-3-Methylpentane							
0.000 00	1071.03	1321.27	0.00	0.056 99	1076.33	1291.73	-4.10
0.000 57	1071.12	1320.92	-0.11	0.060 31	1076.82	1289.57	-4.74
0.001 29	1071.22	1320.48	-0.24	0.070 37	1078.31	1283.07	-6.62
0.002 05	1071.35	1319.97	-0.41	0.077 43	1079.35	1278.51	-7.90
0.002 85	1071.45	1319.50	-0.53	0.082 68	1080.19	1275.01	-8.96
0.003 70	1071.51	1319.13	-0.53	0.106 73	1083.96	1259.22	-13.43
0.004 70	1071.54	1318.78	-0.44	0.148 00	1090.93	1231.57	-21.15
0.005 90	1071.53	1318.47	-0.23	0.202 04	1100.70	1195.14	-30.58
0.007 17	1071.47	1318.27	0.13	0.266 43	1113.19	1151.75	-40.49
0.007 85	1071.45	1318.12	0.27	0.341 03	1128.84	1101.68	-50.04
0.008 57	1071.45	1317.94	0.41	0.404 22	1143.03	1059.72	-56.29
0.010 05	1071.39	1317.64	0.76	0.455 86	1155.27	1025.84	-60.06
0.011 45	1071.41	1317.19	0.93	0.463 50	1157.23	1020.67	-60.71
0.012 98	1071.44	1316.67	1.08	0.500 26	1166.18	997.17	-62.20
0.014 51	1071.51	1316.06	1.15	0.524 59	1172.50	981.33	-63.25
0.016 31	1071.60	1315.30	1.18	0.537 96	1175.72	973.19	-63.19
0.017 79	1071.67	1314.69	1.23	0.570 54	1184.39	952.41	-63.77
0.018 80	1071.76	1314.18	1.16	0.582 61	1187.31	945.33	-63.28
0.021 54	1071.98	1312.81	1.01	0.625 97	1199.19	918.33	-62.77
0.024 27	1072.25	1311.36	0.76	0.692 36	1217.23	879.19	-58.77
0.027 80	1072.57	1309.51	0.49	0.757 78	1235.38	842.33	-51.94
0.028 07	1072.63	1309.29	0.40	0.824 42	1253.97	806.78	-41.80
0.031 90	1073.04	1307.14	-0.05	0.879 28	1269.25	779.09	-31.03
0.037 03	1073.65	1304.12	-0.76	0.920 42	1280.71	759.17	-21.59
0.040 84	1074.13	1301.83	-1.34	0.948 49	1288.48	746.05	-14.44
0.043 61	1074.52	1300.06	-1.86	0.968 16	1293.91	737.04	-9.12
0.051 39	1075.56	1295.25	-3.14	1.000 00	1302.72	722.78	0.00
1-Hexanol-2,2-Dimethylbutane							
0.000 00	998.87	1555.30	0.00	0.066 13	1010.29	1494.87	-19.79
0.001 35	999.20	1553.78	-0.71	0.070 83	1011.50	1489.49	-22.20
0.001 98	999.36	1553.07	-1.05	0.082 66	1014.11	1477.32	-26.82
0.002 63	999.53	1552.31	-1.41	0.095 61	1016.80	1464.60	-31.20
0.003 29	999.67	1551.61	-1.72	0.134 55	1025.88	1424.49	-45.72
0.004 02	999.79	1550.97	-1.93	0.184 68	1038.11	1373.48	-62.64
0.005 03	999.89	1550.30	-1.99	0.249 37	1054.82	1308.80	-81.50
0.006 23	999.95	1549.65	-1.92	0.320 67	1074.42	1239.32	-98.15
0.007 49	1000.01	1548.99	-1.82	0.392 13	1095.32	1171.79	-110.34
0.008 15	1000.04	1548.64	-1.77	0.449 50	1112.95	1119.30	-116.71
0.008 89	1000.09	1548.21	-1.76	0.468 17	1118.76	1102.76	-117.93
0.010 98	1000.20	1547.05	-1.66	0.496 65	1128.05	1077.33	-119.68
0.013 28	1000.44	1545.41	-1.91	0.506 75	1131.22	1068.74	-119.80
0.016 15	1000.77	1543.25	-2.34	0.536 41	1141.10	1042.97	-120.41
0.019 33	1001.22	1540.62	-3.04	0.549 92	1145.48	1031.74	-120.05
0.019 92	1001.32	1540.10	-3.21	0.570 53	1152.52	1014.27	-119.69
0.023 81	1001.94	1536.63	-4.31	0.601 06	1162.85	989.28	-117.94
0.027 73	1002.62	1533.00	-5.54	0.660 73	1183.54	942.02	-111.80

Table I (Continued)

$x$	$u/(m\ s^{-1})$	$\kappa_S/TPa^{-1}$	$\kappa_S^E/TPa^{-1}$	$x$	$u/(m\ s^{-1})$	$\kappa_S/TPa^{-1}$	$\kappa_S^E/TPa^{-1}$
0.031 43	1003.28	1529.52	-6.75	0.735 14	1209.61	886.89	-98.27
0.031 78	1003.37	1529.11	-6.94	0.809 46	1235.84	835.90	-78.43
0.036 82	1004.34	1524.18	-8.78	0.870 19	1257.17	797.32	-57.50
0.042 83	1005.53	1518.20	-11.05	0.920 75	1274.96	767.01	-37.16
0.046 32	1006.17	1514.91	-12.17	0.956 25	1287.38	746.77	-21.24
0.050 37	1007.08	1510.57	-13.99	0.985 31	1297.56	730.72	-7.33
0.059 46	1008.97	1501.39	-17.47	1.000 00	1302.72	722.78	0.00
1-Hexanol-2,3-Dimethylbutane							
0.000 00	1046.66	1389.32	0.00	0.112 00	1063.35	1311.46	-20.15
0.002 31	1047.08	1387.55	-0.63	0.114 43	1063.85	1309.49	-20.81
0.005 23	1047.35	1385.98	-0.76	0.165 26	1073.88	1270.02	-32.43
0.007 06	1047.35	1385.41	-0.42	0.228 00	1087.15	1221.40	-45.34
0.008 01	1047.35	1385.14	-0.22	0.297 99	1103.05	1167.64	-57.59
0.010 58	1047.36	1384.30	0.21	0.355 26	1116.86	1124.33	-65.66
0.014 17	1047.53	1382.72	0.43	0.413 26	1131.59	1081.15	-72.02
0.015 63	1047.65	1381.94	0.37	0.461 88	1144.44	1045.70	-75.74
0.016 99	1047.74	1381.26	0.37	0.490 13	1152.07	1025.53	-77.12
0.019 83	1048.03	1379.59	0.12	0.502 42	1155.55	1016.63	-77.77
0.023 41	1048.41	1377.43	-0.24	0.537 53	1165.37	991.98	-78.60
0.026 43	1048.77	1375.52	-0.64	0.545 83	1167.62	986.39	-78.49
0.027 92	1049.01	1374.42	-0.98	0.568 78	1174.29	970.41	-78.62
0.029 22	1049.16	1373.62	-1.13	0.591 64	1180.77	955.10	-77.99
0.033 16	1049.70	1370.95	-1.81	0.646 53	1196.85	918.86	-75.30
0.038 69	1050.51	1367.04	-2.91	0.704 98	1214.27	881.87	-69.84
0.045 35	1051.54	1362.23	-4.32	0.771 15	1234.14	842.22	-60.25
0.046 67	1051.76	1361.23	-4.65	0.840 87	1255.13	802.98	-46.27
0.052 74	1052.75	1356.76	-6.01	0.896 03	1271.69	773.76	-32.42
0.061 44	1054.20	1350.24	-8.04	0.937 78	1284.12	752.73	-20.31
0.071 75	1055.97	1342.47	-10.45	0.965 93	1292.51	739.00	-11.43
0.074 11	1056.37	1340.70	-10.99	0.985 51	1298.42	729.58	-5.00
0.083 23	1058.01	1333.69	-13.22	1.000 00	1302.72	722.78	0.00
0.095 46	1060.26	1324.22	-16.22				

Table II. Isobaric Thermal Expansivities,  $\alpha_p^*$ , and Molar Isobaric Heat Capacities  $C_p^*$  for the Component Liquids at 298.15 K

component	$\alpha_p^*/$ kK <sup>-1</sup>	$C_p^*/$ (J K <sup>-1</sup> mol <sup>-1</sup> )
1-hexanol	0.870 <sup>a</sup>	240.6 <sup>b</sup>
2-methylpentane	1.426 <sup>c</sup>	193.82 <sup>b</sup>
3-methylpentane	1.396 <sup>c</sup>	190.75 <sup>b</sup>
2,2-dimethylbutane	1.468 <sup>c</sup>	189.12 <sup>b</sup>
2,3-dimethylbutane	1.391 <sup>c</sup>	188.75 <sup>b</sup>

<sup>a</sup> Derived from densities in ref 6. <sup>b</sup> Determined in our laboratory. <sup>c</sup> Derived from densities in ref 7.

compressibilities of 1-hexanol-isomeric hexane mixtures over the whole composition range. The function

$$\kappa_S^E = x(1-x) \sum_{j=1}^n k_j x^{j-1/2} \quad (1)$$

was used to fit the results for  $x > 0.02$ , and the polynomial

$$\kappa_S^E = \sum_{j=1}^n k_j x^j \quad (2)$$

was used for  $x < 0.04$ . For each system, the values of the

coefficients in the two forms were adjusted by the method of least squares with all points weighted equally. The coefficients,  $k_j$ , and the standard deviations,  $\sigma$ , for the representations are listed in Table III. Combination of eq 1 and 2, with the change from one equation to the other made at an appropriate mole fraction within the overlapping region  $0.02 < x < 0.04$ , provides a reasonably smooth representation over the whole composition range.

Plots of the experimental results for  $\kappa_S^E$  and their representations are given in Figures 2 and 3. Previously (2) it was noted that the molar excess volumes,  $V_m^E(0.5)$ , for equimolar mixtures of 1-hexanol with the isomeric hexanes vary nearly linearly with the solubility parameter,  $\delta$ , of the hexane isomer. Since there is a remarkable similarity between the curves for  $\kappa_S^E$  and those for  $V_m^E$ , it is not surprising that there is also a high degree of correlation between  $\kappa_S^E(0.5)$  and  $\delta$  (coefficient of correlation = -0.97).

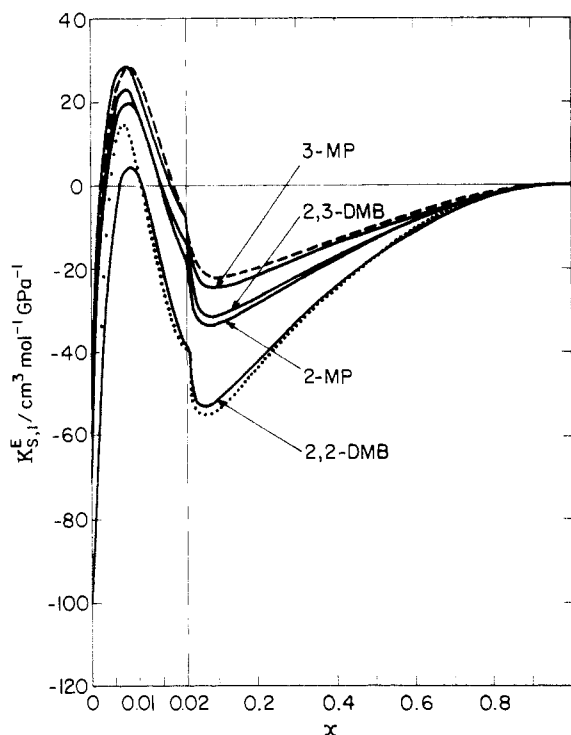
Partial molar excess isentropic compressibilities,  $\kappa_{S^E_i}$ , defined by

$$\kappa_{S^E_i} = -(\partial V_m^E / \partial p)_{T,S} \quad (3)$$

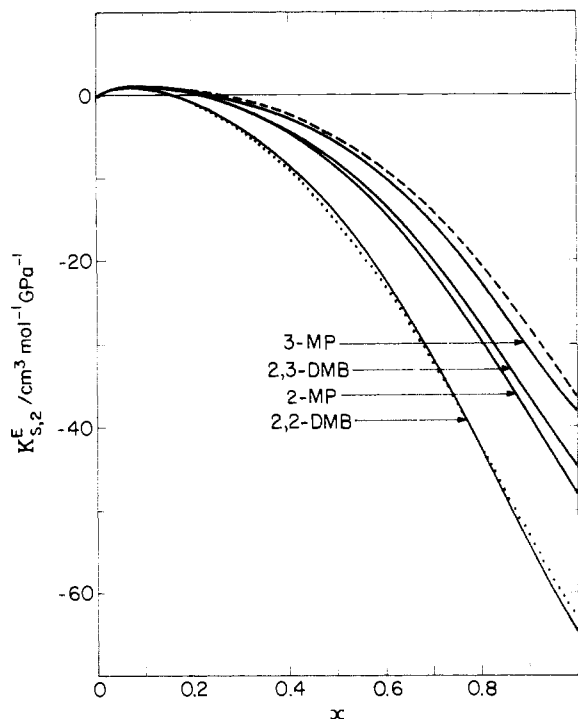
were calculated from the representations of  $\kappa_S^E$  and  $V_m^E$  (2) by the method described in our previous work (1). These re-

Table III. Coefficients,  $k_j$ , and Standard Deviation,  $\sigma$ , for Least-Squares Representations of  $\kappa_S^E$  for 1-Hexanol-Hexane Isomer Mixtures at 298.15 K by Eq 1 in the Range  $0.02 < x < 1$  and by Eq 2 in the Range  $0 < x < 0.04$ 

	2-methylpentane		3-methylpentane		2,2-dimethylbutane		2,3-dimethylbutane	
	eq 1	eq 2	eq 1	eq 2	eq 1	eq 2	eq 1	eq 2
$k_1$	470.743	$-4.9687 \times 10^2$	521.598	$-4.2948 \times 10^2$	383.031	$-8.2228 \times 10^2$	479.460	$-5.3989 \times 10^2$
$k_2$	-5241.66	$9.5307 \times 10^4$	-4981.60	$1.1023 \times 10^5$	-5973.67	$1.2590 \times 10^5$	-4961.06	$1.1931 \times 10^5$
$k_3$	16903.83	$-6.2660 \times 10^6$	15625.48	$-8.7146 \times 10^6$	19878.79	$-8.1058 \times 10^6$	14944.41	$-9.2778 \times 10^6$
$k_4$	-31186.91	$1.6797 \times 10^8$	-28159.15	$3.1704 \times 10^8$	-37718.34	$2.1450 \times 10^8$	-25646.69	$3.3639 \times 10^8$
$k_5$	33085.56	$-1.6281 \times 10^9$	29661.55	$-5.5798 \times 10^9$	41614.19	$-2.0514 \times 10^9$	25481.05	$-5.9478 \times 10^9$
$k_6$	-19058.14		-17389.27	$3.8344 \times 10^{10}$	-25295.86		-14030.25	$4.1317 \times 10^{10}$
$k_7$	4652.37		4426.74		6610.54		3385.98	
$\sigma$	0.11	0.12	0.10	0.07	0.14	0.11	0.05	0.06



**Figure 4.** Partial molar excess isentropic compressibilities,  $K_{S,1}^E$ , of 1-hexanol in 1-hexanol-hexane isomer mixtures at mole fraction,  $x$ , of 1-hexanol and 298.15 K. Different uniform scales are used for  $x < 0.02$  and  $x > 0.02$ . Curves for n-C6 (---) and n-C5 (···) are taken from ref 1.



**Figure 5.** Partial molar excess isentropic compressibilities,  $K_{S,2}^E$ , of hexane isomers in 1-hexanol-hexane isomer mixtures at mole fraction,  $x$ , of 1-hexanol and 298.15 K. Curves for n-C6 (---) and n-C5 (···) are taken from ref 1.

sults are plotted in Figures 4 and 5. Over most of the composition range, the curves for  $\kappa_S^E$  and  $K_S^E$ , shown in Figures 2-5 fall in the following order:

$$n\text{-C6} > 3\text{-MP} > 2,3\text{-DMB} > 2\text{-MP} > 2,2\text{-DMB} > n\text{-C5}$$

In all cases, the curve for 3-MP is close to that for n-C6, and the curve for 2,2-DMB is close to that for n-C5. Qualitatively,

from the point of view of group contributions to the thermodynamic properties under consideration, it appears that the contribution from a  $-\text{C}(\text{CH}_3)_2-$  group is almost the same as that from a  $-\text{CH}_2\text{CH}_2-$  group.

The unusual behavior of the thermodynamic properties in the dilute alkanol region, as shown in Figures 1, 3, and 4, is analogous to that found for alkanol- $n$ -alkane mixtures (1, 8, 9). It is evident from the shapes of the curves that estimates of the properties in this region, obtained by extrapolation from experimental results at higher mole fractions, can be quite erroneous.

#### Acknowledgment

We are indebted to P. J. D'Arcy for determining the molar heat capacities of 1-hexanol and the hexane isomers.

#### Glossary

$C_p$	molar isobaric heat capacity, $\text{J K}^{-1} \text{mol}^{-1}$
$k_j$	coefficients in eq 1 or 2
$K_{S,i}$	partial molar isentropic compressibility of component $i$ in mixture, $\text{cm}^3 \text{mol}^{-1} \text{GPa}^{-1}$
$n$	number of coefficients in eq 1 or 2
$p$	pressure
$T$	thermodynamic temperature, K
$u$	speed of ultrasound, $\text{m s}^{-1}$
$V_i$	partial molar volume of component $i$ in mixture, $\text{cm}^3 \text{mol}^{-1}$
$V_m$	molar volume, $\text{cm}^3 \text{mol}^{-1}$
$x$	mole fraction of 1-hexanol

#### Greek Letters

$\alpha_p$	isobaric thermal expansivity, $\text{kK}^{-1}$
$\kappa_S$	isentropic compressibility, $\text{TPa}^{-1}$
$\sigma$	standard deviation for least-squares fit of $\kappa_S^E$ , $\text{TPa}^{-1}$

#### Superscripts

E	excess value
*	value for pure component

#### Subscripts

1	component 1, 1-hexanol
2	component 2, alkane

**Registry No.** 1-Hexanol, 111-27-3; hexane, 110-54-3; 2-methylpentane, 107-83-5; 3-methylpentane, 96-14-0; 2,2-dimethylbutane, 75-83-2.

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