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# Speeds of Sound and Isentropic Compressibilities of Binary Mixtures Containing Cyclic Ethers and Haloalkanes at 298.15 and 313.15 K

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Speeds of sound of binary mixtures formed by either 1,3-dioxolane or 1,4-dioxane and isomeric chlorobutanes at 298.15 and 313.15 K are reported in this paper. Isentropic compressibilities and isentropic compressibility deviations have been calculated from experimental measurements. Isentropic compressibility deviations have been fitted to a Redlich–Kister equation, and the results have been discussed in terms of molecular interactions and structural effects. Isentropic compressibilities have been estimated at 298.15 K using the Prigogine–Flory–Patterson theory.

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**KEY WORDS:** chlorobutane; cyclic ether; isentropic compressibility; speed of sound.

## 1. INTRODUCTION

A knowledge of the thermodynamic behavior of liquid mixtures has been our main aim during recent years. The investigated mixtures were chosen in order to obtain information about the molecular interactions between their components [1–5]. This is the case for the systems studied in this paper, which contain oxygenated and haloalkane compounds.

Speed-of-sound measurements and calculated isentropic compressibilities as well as isentropic compressibility deviations of 1,3-dioxolane or 1,4-dioxanene with each of several isomers of chlorobutane: 1-chlorobutane, 2-chlorobutane, 2-methyl-1-chloropropane, and 2-methyl-2-chloropropane,

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**Table I.** Densities, $\rho$, and Speeds of Sound, $u$, of the Pure Compounds

| Compound | $T$(K) | $\rho$ ($g \cdot cm^{-3}$) | | $u$ ($m \cdot s^{-1}$) |
|---|---|---|---|---|
| | | Experimental | Literature | |
| 1,3-Dioxolane | 298.15 | 1.0589 | 1.05877 [6] | 1338.8 |
| | 313.15 | 1.0399 | | 1270.8 |
| 1,4-Dioxane | 298.15 | 1.0279 | 1.02797 [7] | 1344.0 |
| | 313.15 | 1.0107 | | 1278.6 |
| 1-Chlorobutane | 298.15 | 0.8808 | 0.88095 [7] | 1119.9 |
| | 313.15 | 0.8638 | | 1057.2 |
| 2-Chlorobutane | 298.15 | 0.8675 | 0.8671 [8] | 1067.8 |
| | 313.15 | 0.8501 | | 1007.1 |
| 2-Methyl-1-chloropropane | 298.15 | 0.8708 | 0.8717 [7] | 1079.8 |
| | 313.15 | 0.8535 | | 1016.6 |
| 2-Methyl-2-chloropropane | 298.15 | 0.8370 | 0.8361 [7] | 984.1 |
| | 313.15 | 0.8183 | | 919.9 |

are presented at 298.15 and 313.15 K. Furthermore, estimation of isentropic compressibilities using the Prigogine–Flory–Patterson theory has been provided and comparisons between the reported and estimated isentropic compressibilities have been performed.

To the best of our knowledge, there are not any literature references for measurements for these systems.

## 2. EXPERIMENTAL

The chemicals provided by Aldrich were: 1,3-dioxolane, 1-chlorobutane, 2-chlorobutane, and 2-methyl-2-chloropropane (better than 99 mol%) and 1,4-dioxane (better than 99.9 mol%). Fluka provided 2-methyl-1-chloropropane (better than 99 mol%). The purity of the liquids was checked by gas chromatography and by measuring their densities. Table I shows experimental values of density for the pure compounds at 298.15 and 313.15 K compared with literature data [6–8] at 298.15 K. No further purification was considered necessary.

Speeds of sound, $u$, of the pure compounds and their mixtures were obtained with an Anton Paar DSA-48 vibrating tube densimeter and sound analyzer. The temperature was automatically kept constant within ±0.01 K. The densities needed to obtain the isentropic compressibilities were also measured with the same apparatus. The precision of the speed of sound and density measurements is $\pm 0.1\, m \cdot s^{-1}$ and $\pm 3 \times 10^{-5}\, g \cdot cm^{-3}$, respectively. The estimated total uncertainty of the speed-of-sound measurements is $\pm 1\,\mathrm{m \cdot s^{-1}}$, while the overall uncertainty of the density measurements is estimated to be $\pm 10^{-5}\,\mathrm{g \cdot cm^{-3}}$. Calibration of the apparatus was carried out with air and deionized double-distilled water. More details of calibration and procedures were reported in a previous paper [9]. Experimental values of the speed of sound of the pure compounds are also reported in Table I.

## 3. RESULTS AND DISCUSSION

Isentropic compressibilities, $\kappa_S$, and isentropic compressibility deviations, $\Delta\kappa_S$, were calculated from experimental densities, $\rho$, and speeds of sound, $u$, using the following equations

$$\kappa_S = \frac{1}{\rho u^2}, \tag{1}$$

$$\Delta\kappa_S = \kappa_S - x_1\kappa_{S,1} - x_2\kappa_{S,2}, \tag{2}$$

where $x_i$ and $\kappa_{S,i}$ are, respectively, the mole fraction and isentropic compressibility of component $i$.

Experimental speeds of sound and estimated isentropic compressibilities, as well as isentropic compressibility deviations, are compiled in Table II, and experimental $\Delta\kappa_S$ values are shown in Figs. 1–4.

Isentropic compressibility deviations have been fitted to a Redlich–Kister type equation

$$\Delta\kappa_S = x_1(1 - x_1)\sum A_i(2x_1 - 1)^i, \tag{3}$$

where $A_i$s are adjustable parameters determined by least-squares optimization. These values are listed in Table III together with the corresponding standard deviations.

For 1,3-dioxolane mixtures, isentropic compressibility deviations are positive except for the mixture of 1,3-dioxolane with 2-methyl-2-chloropropane. Isentropic compressibility deviations decrease in the order: 1-chlorobutane >2-methyl-1-chloropropane > 2-chlorobutane > 2-methyl-2-chloropropane, although the behavior of the mixtures containing 2-chlorobutane and 2-methyl-1-chloropropane is similar. The $\Delta\kappa_S$ values for the mixtures with 1,4-dioxane are lower than for the mixtures containing 1,3-dioxolane. On the other hand, the variation of $\Delta\kappa_S$ with the isomeric chlorobutanes is very similar for both cyclic ethers. The change of $\Delta\kappa_S$ values with temperature is not very significant except for the mixtures containing 2-methyl-2-chloropropane.

These results can be explained in terms of molecular interactions and structural effects. Positive isentropic compressibility deviations are

**Table II.** Speeds of Sound, $u$, Isentropic Compressibilities, $\kappa_S$, and Isentropic Compressibility Deviations, $\Delta\kappa_S$, of the Binary Mixtures for Various Compositions (in mole fraction)

| $x_1$ | $u$ (m·s$^{-1}$) | $\kappa_S$ (TPa$^{-1}$) | $\Delta\kappa_S$(TPa$^{-1}$) | $x_1$ | $u$(m·s$^{-1}$) | $\kappa_S$(TPa$^{-1}$) | $\Delta\kappa_S$ (TPa$^{-1}$) |
|---|---|---|---|---|---|---|---|
| 1,3-Dioxolane (1) + 1-chlorobutane (2) at 298.15 K | | | | | | | |
| 0.0448 | 1123.2 | 894.8 | 6.5 | 0.6120 | 1216.3 | 696.8 | 23.1 |
| 0.0952 | 1127.9 | 881.3 | 12.3 | 0.7006 | 1238.9 | 659.9 | 19.5 |
| 0.1985 | 1141.1 | 849.0 | 18.7 | 0.8169 | 1272.8 | 609.5 | 13.3 |
| 0.2893 | 1154.6 | 818.1 | 22.3 | 0.9089 | 1304.0 | 568.3 | 6.9 |
| 0.3930 | 1172.2 | 780.6 | 24.0 | 0.9592 | 1322.7 | 545.5 | 3.1 |
| 0.4984 | 1191.9 | 741.3 | 24.6 | | | | |
| 1,3-Dioxolane (1) + 2-chlorobutane (2) at 298.15 K | | | | | | | |
| 0.0735 | 1077.3 | 982.7 | 7.2 | 0.5927 | 1190.1 | 734.4 | 10.3 |
| 0.0966 | 1080.9 | 972.7 | 8.4 | 0.7015 | 1222.7 | 679.8 | 8.3 |
| 0.1565 | 1091.0 | 945.9 | 10.6 | 0.8176 | 1263.3 | 619.9 | 4.7 |
| 0.2803 | 1115.0 | 887.4 | 12.1 | 0.8965 | 1294.3 | 579.2 | 2.2 |
| 0.3882 | 1138.5 | 835.0 | 11.9 | 0.9669 | 1324.3 | 543.4 | 0.4 |
| 0.5174 | 1169.9 | 771.7 | 11.1 | | | | |
| 1,3-Dioxolane (1) + 2-methyl-1-chloropropane (2) at 298.15 K | | | | | | | |
| 0.0593 | 1087.2 | 963.5 | 5.7 | 0.6024 | 1198.4 | 721.9 | 12.8 |
| 0.1597 | 1102.5 | 922.9 | 11.1 | 0.7033 | 1227.8 | 673.2 | 10.4 |
| 0.2016 | 1109.6 | 905.2 | 12.6 | 0.8014 | 1260.4 | 624.8 | 6.9 |
| 0.3024 | 1128.5 | 860.9 | 14.4 | 0.9029 | 1298.2 | 574.7 | 3.3 |
| 0.4537 | 1160.9 | 792.0 | 14.8 | 0.9540 | 1318.9 | 549.6 | 1.6 |
| 0.5149 | 1175.5 | 763.5 | 14.3 | | | | |
| 1,3-Dioxolane (1) + 2-methyl-2-chloropropane (2) at 298.15 K | | | | | | | |
| 0.0411 | 992.5 | 1203.8 | −0.9 | 0.5870 | 1153.6 | 793.2 | −25.6 |
| 0.0759 | 1000.3 | 1177.5 | −2.6 | 0.7178 | 1204.6 | 704.0 | −22.3 |
| 0.2013 | 1032.3 | 1078.8 | −12.7 | 0.7911 | 1236.2 | 655.7 | −18.9 |
| 0.3123 | 1063.9 | 992.5 | −20.5 | 0.9100 | 1292.5 | 580.4 | −10.1 |
| 0.3956 | 1089.3 | 929.7 | −24.4 | 0.9575 | 1316.6 | 551.8 | −5.2 |
| 0.4961 | 1121.9 | 856.9 | −26.1 | | | | |
| 1,3-Dioxolane (1) + 1-chlorobutane (2) at 313.15 K | | | | | | | |
| 0.0323 | 1060.3 | 1025.5 | 3.9 | 0.6057 | 1151.0 | 794.0 | 24.9 |
| 0.0986 | 1067.3 | 1003.3 | 10.9 | 0.7016 | 1173.7 | 748.9 | 22.0 |
| 0.1825 | 1077.5 | 972.9 | 17.5 | 0.8062 | 1201.8 | 698.1 | 17.3 |
| 0.2910 | 1092.5 | 931.1 | 23.5 | 0.9005 | 1231.3 | 650.5 | 11.2 |
| 0.3883 | 1107.9 | 891.3 | 26.6 | 0.9550 | 1251.7 | 621.0 | 5.7 |
| 0.4921 | 1126.9 | 846.1 | 27.0 | | | | |
| 1,3-Dioxolane (1) + 2-chlorobutane (2) at 313.15 K | | | | | | | |
| 0.0623 | 1015.7 | 1130.0 | 5.4 | 0.6022 | 1129.2 | 830.2 | 10.3 |
| 0.0916 | 1019.9 | 1115.9 | 7.8 | 0.7090 | 1160.6 | 767.6 | 8.0 |
| 0.1966 | 1036.9 | 1061.8 | 13.0 | 0.8158 | 1195.8 | 705.2 | 5.7 |
| 0.2914 | 1054.4 | 1010.5 | 15.1 | 0.8967 | 1225.8 | 657.7 | 3.9 |
| 0.4126 | 1080.4 | 941.6 | 14.7 | 0.9668 | 1255.0 | 616.1 | 1.9 |
| 0.5090 | 1104.2 | 885.0 | 12.5 | | | | |

**Table II.** (*Continued*)

| $x_1$ | $u$ $(\mathrm{m \cdot s^{-1}})$ | $\kappa_S$ $(\mathrm{TPa^{-1}})$ | $\Delta\kappa_S$ $(\mathrm{TPa^{-1}})$ | $x_1$ | $u$ $(\mathrm{m \cdot s^{-1}})$ | $\kappa_S$ $(\mathrm{TPa^{-1}})$ | $\Delta\kappa_S$ $(\mathrm{TPa^{-1}})$ |
|---|---|---|---|---|---|---|---|
| 1,3-Dioxolane (1) + 2-methyl-1-chloropropane (2) at 313.15 K | | | | | | | |
| 0.0243 | 1020.6 | 1120.9 | 0.2 | 0.5874 | 1128.4 | 832.6 | 15.0 |
| 0.0806 | 1029.6 | 1092.5 | 2.1 | 0.7015 | 1160.8 | 767.9 | 11.7 |
| 0.2037 | 1048.9 | 1033.0 | 8.8 | 0.7952 | 1190.4 | 714.7 | 9.0 |
| 0.2946 | 1064.1 | 988.7 | 13.5 | 0.9168 | 1234.2 | 645.3 | 5.0 |
| 0.3950 | 1083.3 | 937.4 | 16.2 | 0.9713 | 1257.4 | 612.9 | 2.0 |
| 0.4947 | 1105.1 | 884.3 | 16.8 | | | | |
| 1,3-Dioxolane (1) + 2-methyl-2-chloropropane (2) at 313.15 K | | | | | | | |
| 0.0449 | 930.8 | 1398.6 | −7.4 | 0.5953 | 1092.6 | 900.5 | −38.4 |
| 0.0947 | 943.5 | 1348.3 | −15.5 | 0.7576 | 1154.8 | 772.9 | −28.3 |
| 0.1525 | 958.0 | 1292.6 | −22.1 | 0.8053 | 1174.5 | 737.5 | −23.2 |
| 0.2961 | 996.8 | 1159.0 | −33.9 | 0.9210 | 1227.6 | 653.3 | −9.2 |
| 0.3919 | 1024.8 | 1073.8 | −37.8 | 0.9623 | 1249.0 | 623.5 | −4.0 |
| 0.5008 | 1059.6 | 979.5 | −39.7 | | | | |
| 1,4-Dioxane (1) + 1-chlorobutane (2) at 298.15 K | | | | | | | |
| 0.0487 | 1126.1 | 889.9 | 2.4 | 0.5420 | 1217.2 | 710.0 | 3.4 |
| 0.0869 | 1131.5 | 877.2 | 3.7 | 0.6656 | 1246.5 | 663.7 | 2.5 |
| 0.1860 | 1147.0 | 842.3 | 5.2 | 0.7723 | 1274.2 | 623.9 | 1.8 |
| 0.2516 | 1158.4 | 818.4 | 5.4 | 0.8869 | 1307.3 | 581.6 | 1.5 |
| 0.3605 | 1178.9 | 777.8 | 4.8 | 0.9581 | 1329.9 | 554.5 | 0.5 |
| 0.4388 | 1194.8 | 748.5 | 4.2 | | | | |
| 1,4-Dioxane (1) + 2-chlorobutane (2) at 298.15 K | | | | | | | |
| 0.0650 | 1079.4 | 980.1 | −0.2 | 0.6239 | 1216.2 | 705.2 | −11.1 |
| 0.1064 | 1087.5 | 959.7 | −1.1 | 0.7115 | 1243.1 | 664.6 | −10.3 |
| 0.1678 | 1100.3 | 928.8 | −3.0 | 0.8064 | 1273.9 | 621.9 | −8.1 |
| 0.2857 | 1127.1 | 869.0 | −7.1 | 0.9338 | 1318.9 | 566.5 | −3.4 |
| 0.3819 | 1150.6 | 821.0 | −9.7 | 0.9593 | 1328.7 | 555.4 | −2.4 |
| 0.5016 | 1181.7 | 762.9 | −11.2 | | | | |
| 1,4-Dioxane (1) + 2-methyl-1-chloropropane (2) at 298.15 K | | | | | | | |
| 0.0381 | 1086.1 | 968.3 | 0.2 | 0.5589 | 1202.8 | 728.0 | −7.5 |
| 0.0906 | 1095.4 | 944.6 | 0.0 | 0.6553 | 1229.6 | 685.3 | −7.2 |
| 0.1777 | 1112.4 | 904.0 | −1.6 | 0.7742 | 1265.6 | 633.4 | −5.9 |
| 0.2683 | 1131.7 | 861.5 | −3.6 | 0.9020 | 1308.0 | 579.4 | −2.9 |
| 0.3715 | 1155.3 | 813.8 | −5.5 | 0.9483 | 1324.6 | 560.0 | −1.7 |
| 0.4499 | 1174.5 | 777.4 | −6.8 | | | | |
| 1,4-Dioxane (1) + 2-methyl-2-chloropropane (2) at 298.15 K | | | | | | | |
| 0.0259 | 991.0 | 1210.7 | −5.0 | 0.5670 | 1164.0 | 787.5 | −52.1 |
| 0.0812 | 1005.5 | 1163.6 | −13.7 | 0.6656 | 1200.9 | 724.8 | −46.3 |
| 0.1550 | 1027.6 | 1098.2 | −27.8 | 0.7798 | 1247.1 | 656.1 | −35.6 |
| 0.2642 | 1061.0 | 1008.0 | −42.0 | 0.9233 | 1308.9 | 577.5 | −14.4 |
| 0.3736 | 1096.9 | 922.7 | −51.4 | 0.9760 | 1332.8 | 550.6 | −4.7 |
| 0.4613 | 1126.4 | 859.5 | −53.5 | | | | |

**Table II.** (*Continued*)

| $x_1$ | $u$ $(\mathrm{m \cdot s^{-1}})$ | $\kappa_S$ $(\mathrm{TPa^{-1}})$ | $\Delta\kappa_S$ $(\mathrm{TPa^{-1}})$ | $x_1$ | $u$ $(\mathrm{m \cdot s^{-1}})$ | $\kappa_S$ $(\mathrm{TPa^{-1}})$ | $\Delta\kappa_S$ $(\mathrm{TPa^{-1}})$ |
|---|---|---|---|---|---|---|---|
| 1,4-Dioxane (1) + 1-chlorobutane (2) at 313.15 K | | | | | | | |
| 0.0528 | 1065.1 | 1013.3 | 0.3 | 0.6059 | 1166.8 | 778.1 | 3.2 |
| 0.0706 | 1067.8 | 1005.8 | 0.4 | 0.6864 | 1186.0 | 743.3 | 3.1 |
| 0.1864 | 1086.0 | 957.0 | 1.5 | 0.7962 | 1214.6 | 695.6 | 2.6 |
| 0.2770 | 1101.2 | 918.7 | 2.3 | 0.9124 | 1248.9 | 644.5 | 1.6 |
| 0.3940 | 1122.6 | 869.1 | 2.9 | 0.9479 | 1260.5 | 628.7 | 1.1 |
| 0.5068 | 1145.1 | 820.7 | 3.2 | | | | |
| 1,4-Dioxane (1) + 2-chlorobutane (2) at 313.15 K | | | | | | | |
| 0.0786 | 1021.2 | 1114.8 | −1.3 | 0.5891 | 1142.4 | 818.5 | −14.6 |
| 0.1045 | 1026.0 | 1099.9 | −1.9 | 0.6624 | 1162.7 | 779.9 | −12.5 |
| 0.1775 | 1041.0 | 1056.2 | −5.1 | 0.7942 | 1201.7 | 712.7 | −6.6 |
| 0.2634 | 1060.0 | 1004.7 | −9.0 | 0.9090 | 1240.7 | 654.2 | −1.5 |
| 0.3864 | 1089.3 | 932.1 | −13.3 | 0.9485 | 1256.2 | 633.3 | −0.5 |
| 0.4852 | 1114.5 | 875.7 | −15.0 | | | | |
| 1,4-Dioxane (1) + 2-methyl-1-chloropropane (2) at 313.15 K | | | | | | | |
| 0.0415 | 1024.2 | 1110.1 | −1.8 | 0.6042 | 1151.4 | 802.5 | −11.9 |
| 0.0903 | 1033.4 | 1082.5 | −3.5 | 0.7014 | 1177.0 | 755.0 | −8.0 |
| 0.1919 | 1053.4 | 1025.7 | −6.6 | 0.8136 | 1208.4 | 701.9 | −1.8 |
| 0.2910 | 1074.7 | 970.3 | −9.6 | 0.9176 | 1242.8 | 650.9 | 2.1 |
| 0.4693 | 116.9 | 872.7 | −13.0 | 0.9550 | 1257.6 | 631.1 | 2.1 |
| 0.5061 | 1126.2 | 853.1 | −13.2 | | | | |
| 1,4-Dioxane (1) + 2-methyl-2-chloropropane (2) at 313.15 K | | | | | | | |
| 0.0533 | 935.3 | 1382.2 | −17.2 | 0.5822 | 1106.3 | 885.4 | −70.3 |
| 0.0898 | 945.6 | 1342.2 | −26.7 | 0.7006 | 1151.0 | 797.4 | −58.9 |
| 0.2057 | 980.7 | 1218.7 | −52.9 | 0.8139 | 1196.0 | 720.4 | −40.9 |
| 0.2998 | 1011.0 | 1124.7 | −68.0 | 0.8414 | 1206.5 | 703.9 | −34.3 |
| 0.4008 | 1044.1 | 1032.5 | −75.4 | 0.9540 | 1256.0 | 633.6 | −10.2 |
| 0.4916 | 1074.5 | 956.7 | −75.0 | | | | |

due to the breaking of interactions and the corresponding disruption of molecular order in the pure compounds [10]. Interactions between the molecules of cyclic ethers or chlorobutanes are broken in the mixing process; the breaking of strong dipole–dipole interactions in the 1,3-dioxolane, which can be considered as a polar fluid in contrast with 1,4-dioxane which is a nonpolar fluid [11], leads to higher positive $\Delta\kappa_S$ values for the mixtures containing 1,3-dioxolane. Although new donor–acceptor interactions are formed between the oxygen and chloride atoms, this contribution is less important. Structural effects like interstitial accommodation and changes in free volume also play an important role as is demonstrated by the different behavior of the isomeric chlorobutanes:

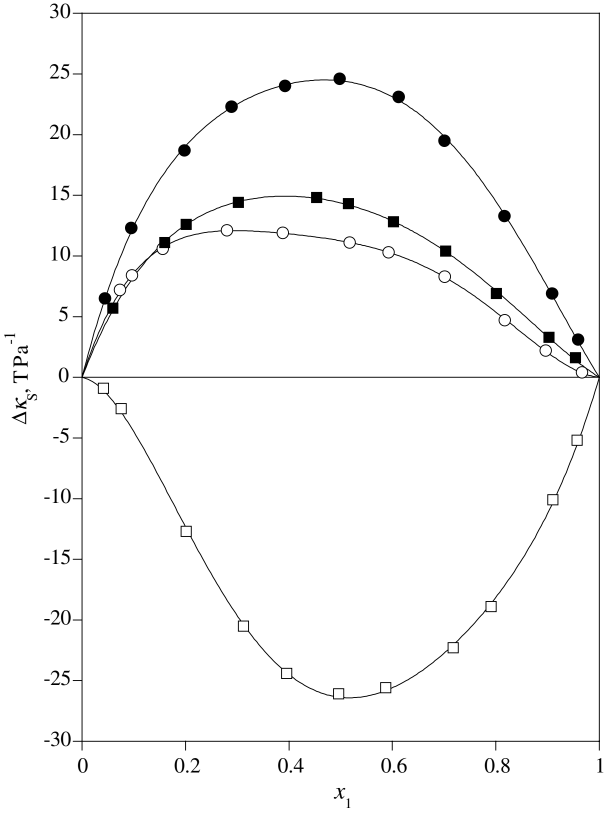

**Fig. 1.** Isentropic compressibility deviations, $\Delta\kappa_S$, at 298.15 K of binary mixtures of 1,3-dioxolane (1) with 1-chlorobutane (2) (●), 2-chlorobutane (2) (○), 2-methyl-1-chloropropane (2) (■), 2-methyl-2-chloropropane (2) (□).

positive $\Delta\kappa_S$ values for the mixtures with 1-chlorobutane that have a linear structure, and on the other hand, negative $\Delta\kappa_S$ values for the mixtures with 2-methyl-2-chloropropane which represent a globular structure. Finally, the behavior of 2-chlorobutane and 2-methyl-1-chloropropane systems is situated between these two extreme situations.

## 4. THEORY

Oswall [14] extended the Prigogine–Flory–Patterson theory to estimate the isentropic compressibilities and speeds of sound of liquid mixtures. At

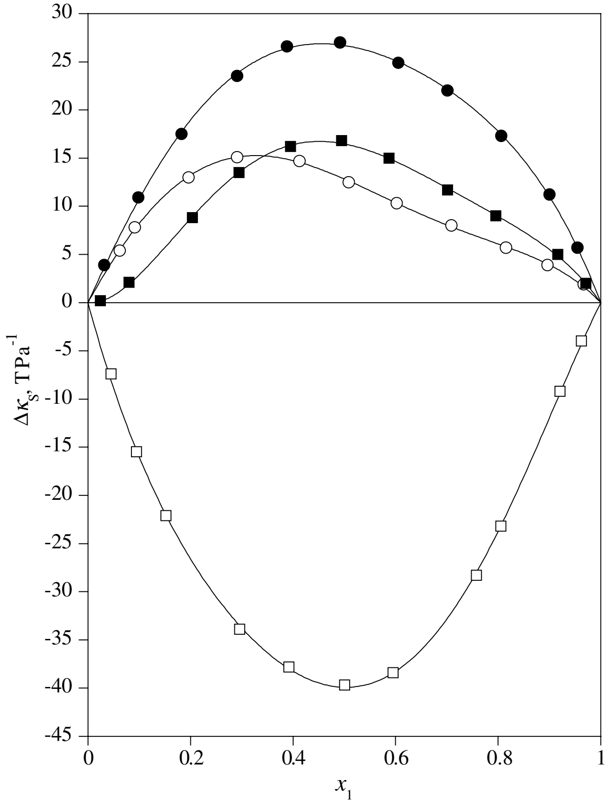

**Fig. 2.** Isentropic compressibility deviations, $\Delta\kappa_S$, at 313.15 K of binary mixtures of 1,3-dioxolane (1) with 1-chlorobutane (2) (●), 2-chlorobutane (2) (○), 2-methyl-1-chloropropane (2) (■), 2-methyl-2-chloropropane (2) (□).

a given temperature, $T$, the P–F–P theory can be used to calculate the molar volumes, $V$, the molar heat capacities, $C_P$ of a liquid mixture if the interaction parameter, $\chi_{12}$, is known. The terms $(\partial V/\partial T)_P$ and $(\partial V/\partial P)_T$ can be also calculated by means of the following equations

$$(\partial V/\partial P)_T = \frac{(-\tilde{V}^{7/3} + 2\tilde{V}^2 - 2\tilde{V}^{5/3})}{((4/3) - \tilde{V}^{1/3})} \frac{V^* T^*}{P^* T}, \tag{4}$$

$$(\partial V/\partial T)_P = \frac{\tilde{V}(\tilde{V}^{1/3} - 1)}{((4/3) - \tilde{V}^{1/3})} \frac{V^*}{T}, \tag{5}$$

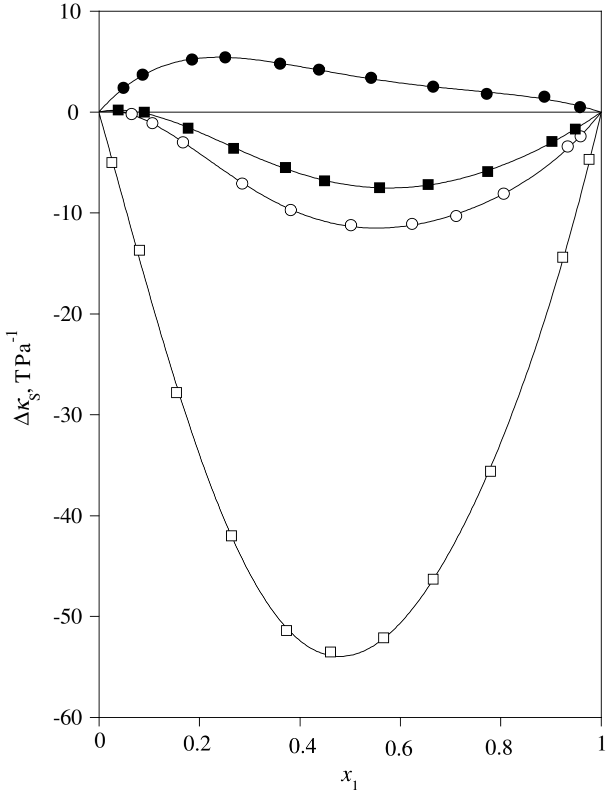

**Fig. 3.** Isentropic compressibility deviations, $\Delta\kappa_S$, at 298.15 K of binary mixtures of 1,4-dioxane (1) with 1-chlorobutane (2) (●), 2-chlorobutane (2) (○), 2-methyl-1-chloropropane (2) (■), 2-methyl-2-chloropropane (2) (□).

where $V^*$, $P^*$, and $T^*$ are the characteristic volume, pressure, and temperature of the mixture, respectively, and $\tilde{V}$ is the corresponding reduced volume.

From all these quantities the isentropic compressibility, $\kappa_S = -V^{-1} (\partial V/\partial P)_S$ can be obtained using the following thermodynamic relation

$$(\partial V/\partial P)_S = (\partial V/\partial P)_T + TC_P^{-1}(\partial V/\partial T)_P^2 \tag{6}$$

and finally the isentropic compressibility is related to the speed of sound, $u$, by Eq. (1).

Flory parameters [15,16] of the pure compounds along with their physical properties are given in Table IV. Thermal expansion coefficients,

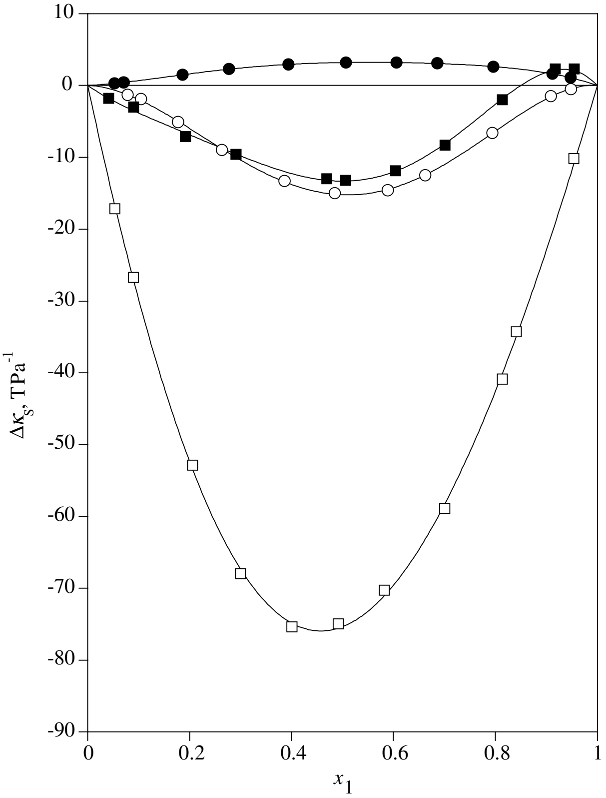

**Fig. 4.** Isentropic compressibility deviations, $\Delta\kappa_S$, at 313.15 K of binary mixtures of 1,4-dioxane (1) with 1-chlorobutane (2) (●), 2-chlorobutane (2) (○), 2-methyl-1-chloropropane (2) (■), 2-methyl-2-chloropropane (2) (□).

$\alpha$, were derived from measured densities in this laboratory. Isothermal compressibilities, $\kappa_T$, were calculated from thermal expansion coefficients, experimental isentropic compressibilities, and molar heat capacities [2,17]. The number of contact sites per segment of a molecule, $s$, has been estimated using Bondi's method [18].

In this work the interaction parameter for each mixture was obtained by fitting the P–F–P theory to the corresponding experimental equimolar $V^E$ values [19,20]. Once the interaction parameter is obtained, the isentropic compressibility and the speed of sound can be estimated.

Table V gives the estimated and experimental equimolar $u$ and $\kappa_S$ values along with the interaction parameter. Estimated values for speeds

**Table III.** Redlich–Kister Parameters, $A_i$s, and Standard Deviations, $\sigma$, for $\Delta\kappa_S$ ($TPa^{-1}$) at 298.15 and 313.15 K

| System | $T$ (K) | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $\sigma$ |
|---|---|---|---|---|---|---|
| 1,3-Dioxolane + | | | | | | |
| 1-Chlorobutane | 298.15 | 97.7 | −9.5 | 19.7 | −39.4 | 0.3 |
| | 313.15 | 106.7 | −16.1 | 22.3 | 27.9 | 0.3 |
| 2-Chlorobutane | 298.15 | 45.0 | −14.9 | 22.0 | −47.9 | 0.1 |
| | 313.15 | 51.3 | −46.6 | 25.1 | 26.2 | 0.2 |
| 2-Methyl-1-chloropropane | 298.15 | 57.5 | −20.4 | 11.2 | −21.4 | 0.1 |
| | 313.15 | 65.9 | −20.7 | −29.9 | 60.9 | 0.2 |
| 2-Methyl-2-chloropropane | 298.15 | −105.5 | −8.9 | 28.7 | −59.3 | 0.3 |
| | 313.15 | −159.7 | −2.0 | 6.8 | 47.0 | 0.4 |
| 1,4-Dioxane + | | | | | | |
| 1-Chlorobutane | 298.15 | 14.5 | −16.7 | 22.1 | −4.2 | 0.1 |
| | 313.15 | 12.8 | 2.2 | 1.2 | 8.3 | 0.0 |
| 2-Chlorobutane | 298.15 | −45.3 | −13.0 | 18.7 | −23.7 | 0.1 |
| | 313.15 | −60.9 | −5.1 | 61.9 | 8.8 | 0.1 |
| 2-Methyl-1-chloropropane | 298.15 | −29.0 | −14.3 | 16.9 | −8.4 | 0.1 |
| | 313.15 | −52.9 | 0.3 | 65.1 | 61.0 | 0.1 |
| 2-Methyl-2-chloropropane | 298.15 | −215.4 | 19.6 | 19.4 | −37.5 | 0.5 |
| | 313.15 | −301.5 | 55.3 | 13.3 | −11.9 | 0.8 |

**Table IV.** Physical Properties and Flory Parameters of the Pure Compounds at 298.15 K

| Compound | $\alpha$ ($mK^{-1}$) | $\kappa_T$ ($TPa^{-1}$) | $\tilde{V}$ | $P^*$ ($J \cdot cm^{-3}$) | $s$ ($Å^{-1}$) |
|---|---|---|---|---|---|
| 1,3-Dioxolane | 1.164 | 758.1 | 1.280 | 750 | 1.23 |
| 1,4-Dioxane | 1.132 | 738.0 [8] | 1.274 | 742 | 1.25 |
| 1-Chlorobutane | 1.216 | 1200.7 | 1.290 | 502 | 1.42 |
| 2-Chlorobutane | 1.313 | 1355.5 | 1.309 | 495 | 1.41 |
| 2-Methyl-1-chloropropane | 1.183 | 1269.2 | 1.284 | 458 | 1.42 |
| 2-Methyl-2-chloropropane | 1.437 | 1656.2 | 1.331 | 458 | 1.45 |

of sound and isentropic compressibilities are better for 1,3-dioxolane mixtures (nearly 1.5% deviation from experimental data for speed of sound and 2.5% deviation from experimental isentropic compressibilities) than for 1,4-dioxane systems whose deviations in speed of sound are 2.5% from experimental values and nearly 5% for isentropic compressibilities.

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**Table V.** Interaction Parameters, $\chi_{12}$, and Calculated and Experimental Equimolar Speeds of Sound and Isentropic Compressibilities at 298.15 K

| System | $\chi_{12}$ $(\mathrm{J \cdot cm^{-3}})$ | $u_{\mathrm{cal}}(\mathrm{m \cdot s^{-1}})$ | $u_{\mathrm{exp}}(\mathrm{m \cdot s^{-1}})$ | $\kappa_{\mathrm{Scal}}(\mathrm{TPa^{-1}})$ | $\kappa_{\mathrm{Sexp}}(\mathrm{TPa^{-1}})$ |
|---|---|---|---|---|---|
| 1,3-Dioxolane + | | | | | |
| 1-Chlorobutane | 20.4 | 1211.1 | 1191.8 | 717.8 | 740.9 |
| 2-Chlorobutane | 14.2 | 1184.5 | 1164.7 | 755.4 | 780.5 |
| 2-Methyl-1-chloropropane | 4.4 | 1192.1 | 1171.6 | 745.0 | 770.4 |
| 2-Methyl-2-chloropropane | −0.5 | 1142.7 | 1120.8 | 825.2 | 854.4 |
| 1,4-Dioxane + | | | | | |
| 1-Chlorobutane | 25.2 | 1237.0 | 1207.6 | 691.8 | 726.0 |
| 2-Chlorobutane | 24.5 | 1210.7 | 1181.1 | 727.0 | 763.8 |
| 2-Methyl-1-chloropropane | 11.7 | 1218.9 | 1187.1 | 716.2 | 754.9 |
| 2-Methyl-2-chloropropane | 11.2 | 1172.5 | 1139.8 | 787.0 | 832.7 |

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