Ultrasonic Speeds and Isentropic Compressibilities of 1,2-Dichlorobenzene + Methyl Ethyl Ketone + 1-Alkanols at 303.15 K

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The densities and ultrasonic speeds of ternary liquid mixtures were measured at 303.15 K. The mixtures were 1,2-dichlorobenzene + methyl ethyl ketone + 1-propanol, + 1-butanol, + 1-pentanol, and + 1-hexanol. Isentropic compressibilities have been computed from measured speeds of sound and densities calculated from measured excess volumes. The deviation in the isentropic compressibility does not exhibit a regular trend in the four ternary mixtures.

Introduction

This work forms part of a study on the thermodynamic properties of ternary mixtures (*1*) and involves the calculation of isentropic compressibilities from measured speeds of sound and densities calculated from measured excess volumes. The third component (1-alkanols) was chosen because it provides a change in both the nature and degree of interaction between pairs of molecules. Results are given for the isentropic compressibility for 1,2-dichlorobenzene + methyl ethyl ketone + 1-propanol, + 1-butanol, + 1-pentanol, and + 1-hexanol. Excess volumes of these ternary liquid mixtures were reported in our earlier paper (*1*).

Purification of Materials

All chemicals were analytical grade. 1,2-Dichlorobenzene, methyl ethyl ketone, and 1-alkanols were purified by the methods described in our earlier paper (*1*). The purity of the samples was checked by comparing the measured densities with those reported in the literature (*2*). The densities of pure liquids were measured with a bicapillary type pycnometer (*3*) with an accuracy of 2 parts in 10^5. The speed of sound was measured with a single-crystal interferometer at a frequency of 4 MHz. The measured densities and sound velocities and those reported in the literature are given in Table 1.

Experimental Procedure

Isentropic compressibilities were computed from speeds of sound and densities evaluated from measured excess volumes. Excess volumes were measured as a function of composition using the dilatometric method described earlier (*4*). Ultrasonic sound velocities were measured with a single-crystal interferometer at a frequency of 4 MHz. The values are accurate to ±0.15%. All the measurements were made at constant temperature employing a thermostat that could maintain the temperature to (303.15 ± 0.01) K. Isentropic compressibilities calculated from speeds of sound and densities are accurate to ±2 TPa^{-1}.

Results and Discussion

Isentropic compressibilities of ternary mixtures, k_{s123}, were calculated using the expression

$$k_{s123} = u^{-2}\rho^{-1} \tag{1}$$

where u and ρ denote the speed of sound and density, respectively.

The densities for ternary mixtures were calculated from the relation

$$\rho = \frac{x_1M_1 + x_2M_2 + x_3M_3}{V + V^{E}_{123}} \tag{2}$$

where x_1, x_2, and x_3 and M_1, M_2, and M_3 denote the mole fractions and molecular weights of 1,2-dichlorobenzene, methyl ethyl ketone, and 1-alkanol, respectively. V and V^{E}_{123} represent the ideal molar volume and experimental molar excess volume, respectively.

The deviation in isentropic compressibility, δk_{s123}, for ternary mixtures was computed employing the relation

$$\delta k_{s123} = k_{s123} - k^{id}_{s123} \tag{3}$$

where k_{s123} and k^{id}_{s123} are the isentropic compressibilities of the real and ideal mixtures, respectively. The ideal isentropic compressibility was assumed to be additive in

Table 1. Densities (ρ) and Ultrasonic Speeds (u) of Pure Components at 303.15 K

component	ρ/(g·cm^{-3}) obsd	ρ/(g·cm^{-3}) lit. (*2*)	u/(m·s^{-1}) obsd	u/(m·s^{-1}) lit.
1,2-dichlorobenzene	1.299 20	1.299 20	1264	1261 (*6*)
methyl ethyl ketone	0.794 57	0.794 52	1169	1170 (*7*)
1-propanol	0.796 02	0.796 00	1192	1191 (*8*)
1-butanol	0.802 03	0.802 06	1227	1224 (*8*)
1-pentanol	0.807 64	0.807 64	1258	1256 (*8*)
1-hexanol	0.812 05	0.812 01	1286	1288 (*8*)

Table 2. Volume Fractions (ϕ_1) of 1,2-Dichlorobenzene, Densities (ρ), Speeds of Sound (u), Isentropic Compressibilities (k_s), and Deviations in isentropic Compressibility (δk_s) for 1,2-Dichlorobenzene + Methyl Ethyl Ketone at 303.15 K

ϕ_1	ρ/(g·cm^{-3})	u/(m·s^{-1})	k_s/TPa^{-1}	δk_s/TPa^{-1}
0.0000	0.794 57	1169	921	0
0.0805	0.836 42	1174	867	−19
0.1904	0.893 23	1186	796	−41
0.2524	0.925 17	1190	763	−47
0.3093	0.954 35	1196	733	−52
0.4312	1.016 44	1208	674	−58
0.5900	1.096 56	1227	606	−56
0.7161	1.159 49	1238	563	−44
0.8187	1.210 24	1249	530	−32
0.9233	1.261 75	1259	500	−16
1.0000	1.299 20	1264	482	0

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Table 3. Values of Parameters b_0, b_1, and b_2 and the Standard Deviation $\sigma(\delta k_s)$ for Binary Systems at 303.15 K

system	b_0/TPa^{-1}	b_1/TPa^{-1}	b_2/TPa^{-1}	$\sigma(\delta k_s)$/TPa^{-1}
1,2-dichlorobenzene + methyl ethyl ketone	−232.5	27.0	−13.7	1
1,2-dichlorobenzene + 1-propanol	−131.0	92.0	12.6	0
1,2-dichlorobenzene + 1-butanol	−141.9	97.2	−19.3	1
1,2-dichlorobenzene + 1-pentanol	−87.0	16.0	−99.1	1
1,2-dichlorobenzene + 1-hexanol	−70.2	33.2	−39.5	1

Table 4. Experimental Values of the Isentropic Compressibility for 1,2-Dichlorobenzene (1) + Methyl Ethyl Ketone (2) + 1-Alkanol (3) at 303.15 K

ϕ_1	ϕ_2	ρ/(g·cm^{-3})	u/(m·s^{-1})	k_{s123}/TPa^{-1}	δk_{s123}/TPa^{-1}	δk_{s123}(bc)/TPa^{-1}	dk_{s123}/TPa^{-1}
1,2-Dichlorobenzene (1) + Methyl Ethyl Ketone (2) + 1-Propanol (3)							
0.2225	0.0707	0.910 23	1219	739	−58	−31	−27
0.2154	0.1672	0.907 10	1217	744	−60	−30	−30
0.1505	0.2871	0.873 77	1203	791	−43	−24	−19
0.1597	0.3245	0.878 47	1202	788	−44	−26	−18
0.1634	0.4738	0.880 24	1195	795	−41	−28	−13
0.1622	0.5231	0.879 53	1194	798	−40	−28	−12
0.1867	0.6053	0.891 99	1194	786	−45	−33	−12
0.2108	0.7002	0.904 18	1192	778	−49	−39	−10
0.1330	0.8276	0.863 80	1183	827	−34	−29	−5
1,2-Dichlorobenzene (1) + Methyl Ethyl Ketone (2) + 1-Butanol (3)							
0.2340	0.0674	0.920 12	1224	725	−28	−35	7
0.2022	0.1174	0.903 80	1223	740	−29	−32	3
0.1498	0.2129	0.876 51	1220	766	−30	−26	−4
0.1570	0.2715	0.879 83	1218	766	−33	−27	−6
0.1714	0.3712	0.886 22	1214	766	−37	−29	−8
0.1647	0.4678	0.882 08	1210	774	−41	−28	−13
0.1643	0.5498	0.881 26	1203	784	−38	−29	−9
0.2276	0.7022	0.912 74	1192	771	−44	−42	−2
0.1567	0.7676	0.876 25	1185	812	−33	−32	−1
1,2-Dichlorobenzene (1) + Methyl Ethyl Ketone (2) + 1-Pentanol (3)							
0.2132	0.0770	0.912 68	1223	732	3	−22	25
0.1701	0.2318	0.890 02	1212	765	2	−21	23
0.1645	0.3266	0.886 38	1209	772	−6	−21	15
0.0965	0.4501	0.850 59	1207	807	−9	−15	6
0.1680	0.5411	0.885 72	1203	780	−27	−27	0
0.2059	0.6191	0.903 82	1199	769	−37	−34	−3
0.2275	0.7068	0.913 33	1193	769	−43	−41	−2
0.1258	0.8392	0.860 38	1182	832	−29	−28	−1
1,2-Dichlorobenzene (1) + Methyl Ethyl Ketone (2) + 1-Hexanol (3)							
0.2247	0.0794	0.921 84	1263	680	−20	−19	−1
0.1903	0.1417	0.904 02	1256	701	−19	−18	−1
0.1571	0.2444	0.885 88	1246	727	−20	−18	−2
0.1511	0.3325	0.881 44	1238	740	−24	−19	−5
0.1147	0.4117	0.861 90	1231	766	−21	−16	−5
0.1483	0.4908	0.877 38	1222	763	−29	−22	−7
0.1614	0.5260	0.883 37	1219	762	−33	−25	−8
0.2062	0.6098	0.904 33	1214	750	−48	−34	−14
0.1347	0.7651	0.866 06	1195	809	−35	−27	−8

terms of the volume fraction and was calculated using the relation

$$k_{s123}^{id} = \phi_1 k_{s1} + \phi_2 k_{s2} + \phi_3 k_{s3} \qquad (4)$$

where ϕ_1, ϕ_2, and ϕ_3 denote the volume fractions and k_{s1}, k_{s2}, and k_{s3} the isentropic compressibilities of the pure components 1,2-dichlorobenzene, methyl ethyl ketone, and 1-alkanol, respectively.

The quantity dk_{s123} has been computed using the relation

$$\mathrm{d}k_{s123} = \delta k_{s123} - \delta k_{s123}(\mathrm{bc}) \qquad (5)$$

where δk_{s123} is the deviation in isentropic compressibility calculated using eq 3 and δk_{s123}(bc) is the deviation in compressibility calculated from binary data using the relation

$$\delta k_{s123}(\mathrm{bc}) = \delta k_{s12} + \delta k_{s13} + \delta k_{s23} \qquad (6)$$

where δk_{s12}, δk_{s13}, and δk_{s23} denote deviations in isentropic compressibilities of the constituent binary mixtures. δk_{sij} for a binary mixture was estimated using the smoothing equation

$$\delta k_{sij} = \phi_i \phi_j [b_0 + b_1(\phi_i - \phi_j) + b_2(\phi_i - \phi_j)^2] \qquad (7)$$

where b_0, b_1, and b_2 are constants obtained by the method of least squares.

The dk_{s123} values were fitted to the polynomial

$$\mathrm{d}k_{s123} = \phi_1\phi_2\phi_3[A + B\phi_1(\phi_2 - \phi_3) + C\phi_1^{\,2}(\phi_2 - \phi_3)^2] \qquad (8)$$

where ϕ_1, ϕ_2, and ϕ_3 are the volume fractions of components 1, 2, and 3, respectively. The values of the adjustable parameters A, B, and C are obtained by the least squares method and are given in Table 5 along with the standard deviation σ(dk_{s123}).

The binary parameters used in eq 7 for the isentropic compressibility for 1,2-dichlorobenzene + 1-alkanols and methyl ethyl ketone + 1-alkanols were taken from the literature (*5*−*7*). The isentropic compressibility data for 1,2-dichlorobenzene + methyl ethyl ketone were also calculated. The results are presented in Table 2 and are

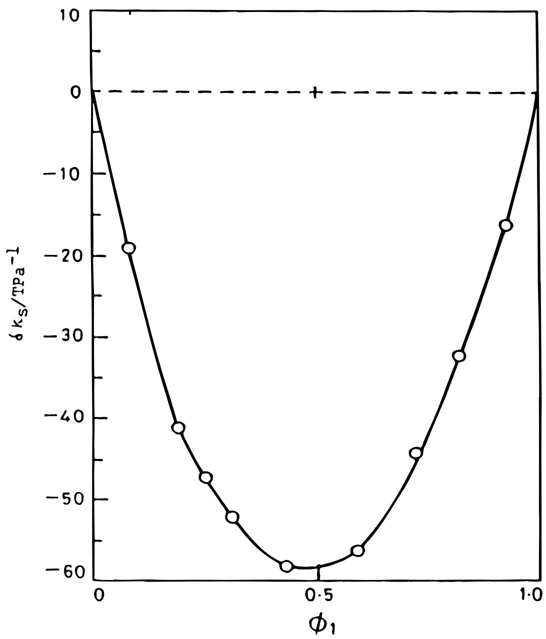

Figure 1. Deviation in isentropic compressibility (δk_s) plotted against the volume fraction (ϕ_1) of 1,2-dichlorobenzene with methyl ethyl ketone at 303.15 K.

graphically represented in Figure 1. The binary parameters are given in Table 3 along with standard deviations. The binary parameters for methyl ethyl ketone + 1-alkanols at 303.15 K were not included in Table 3, as the deviations were zero with the estimated uncertainty.

The isentropic compressibility, k_{s123}, and deviation in isentropic compressibility, δk_{s123}, for the ternary mixtures are given in columns 5 and 6 of Table 4. The deviation in isentropic compressibility, computed from binary data, δk_{s123}(bc), are given in column 7 of Table 4. Finally the values of dk_{s123} are given in column 8 of the Table 4.

Table 5. Values of Ternary Parameters *A*, *B*, and *C* and the Standard Deviation $\sigma(dk_{s123})$ for 1,2-Dichlorobenzene (1) + Methyl Ethyl Ketone (2) + 1-Alkanol (3) at 303.15 K

1-alkanol	A/TPa^{-1}	B/TPa^{-1}	C/TPa^{-1}	$\sigma(dk_{s123})$/TPa^{-1}
1-propanol	−497	4799	−57 287	2
1-butanol	−385	−2348	27 604	2
1-pentanol	294	−8670	36 210	1
1-hexanol	−224	−3505	−18 124	1

The dk_{s123} values are negative over the composition range for mixtures containing 1-propanol and 1-hexanol. The dk_{s123} values exhibit inversion in sign for the mixtures containing 1-butanol and 1-pentanol. dk_{s123} does not change in a regular manner with respect to the chain length of the 1-alkanols.

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