Articles

Speed of Sound of 1,3-Dichlorobenzene + Methyl Ethyl Ketone + 1-Alkanols at 303.15 K

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Isentropic compressibilities of four ternary mixtures (1,3-dichlorobenzene + methyl ethyl ketone + 1-propanol, + 1-butanol, + 1-pentanol, and + 1-hexanol) were determined from speed of sound measurements at 303.15 K. The deviation in isentropic compressibility was also computed. The deviation is, in general, negative for all mixtures. Speed of sound data were compared with those predicted by free length theory and collision factor theory. The predictive expressions give a rough estimate of the property for all the mixtures.

Introduction

A survey of the literature shows few measurements on the isentropic compressibilities of ternary mixtures of nonelectrolytes though measurements have been made on a large number of binary mixtures. Hence, we present here results for the compressibility of four ternary mixtures. 1,3-Dichlorobenzene and methyl ethyl ketone were the common components and 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol were the noncommon components. The speed of sound results were analyzed in terms of the free length theory (FLT) of Jacobson (1952) and the collision factor theory (CFT) of Schaaffs (1963, 1974).

Experimental Details

All chemicals used were of analytical grade. 1,3-Dichlorobenzene was washed successively with 10% sodium hydroxide solution and then with water until the washings were neutral, dried, and fractionated, described by Riddick and Bunger (1970). Methyl ethyl ketone and 1-alkanols were purified by the methods described in our earlier paper (Sekar et al., 1993). The purity of the compounds was checked by comparing the measured densities with those reported in the literature (Timmermans, 1950). The densities of pure liquids were measured with a bicapillary type pycnometer (Rao, 1974), which offers an accuracy of 2 parts in 10^5. Ultrasonic speeds were measured with a single-crystal ultrasonic interferometer at a frequency of 4 MHz at 303.15 K. They are accurate to ±0.15%. All the measurements were made at a constant temperature employing a thermostat, which could be maintained to ±0.01 K.

Isentropic compressibilities were computed from the measured speed of sound and density (evaluated from measured excess volumes). Excess volume was measured as a function of composition using the dilatometric method described earlier (Naidu and Naidu, 1981). Isentropic compressibilities are accurate to ±2 TPa^{-1}. The measured densities and speeds of sound of the pure compounds and those reported in the literature are given in Table 1.

Results and Discussion

Speeds of sound for the four ternary mixtures were analyzed in terms of the free length theory of Jacobson and

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

component	ρ/(g·cm^{-3}) obsd	ρ/(g·cm^{-3}) lit.	u/(m·s^{-1}) obsd	u/(m·s^{-1}) lit.
1,3-dichlorobenzene	1.277 18	1.277 18[a]	1244	1243[a]
methyl ethyl ketone	0.794 57	0.794 52[b]	1169	1170[d]
1-propanol	0.796 02	0.796 00[c]	1192	1192[e]
1-butanol	0.802 03	0.802 06[b]	1227	1232[e]
1-pentanol	0.807 64	0.807 64[b]	1258	1256[f]
1-hexanol	0.812 05	0.812 01[b]	1286	1288[e]

[a] Vijayalakshmi and Naidu (1995). [b] Timmermans (1950). [c] Riddick and Bunger (1970). [d] Venkateswarlu and Raman (1985). [e] Dharmaraju et al. (1982). [f] Rao and Naidu (1976).

Table 2. Values of the Molar Volume (V), Molar Volume at Absolute Zero (V_0), Available Volume (V_a), Free Length (L_f), Surface Area (Y), Collision Factor (S), and Molecular Radius (r_m) of the Pure Components at 303.15 K

component	V/(cm^3·mol^{-1})	V_0/(cm^3·mol^{-1})	V_a/(cm^3·mol^{-1})	L_f	Y	S	r_m/Å
1,3-dichlorobenzene	115.097	96.553	18.544	0.4488	82.638	1.5748	2.8246
methyl ethyl ketone	90.754	70.647	20.107	0.6055	66.413	1.6456	2.5188
1-propanol	75.501	58.823	16.678	0.5933	56.220	1.7319	2.3441
1-butanol	92.412	73.278	19.134	0.5742	66.646	1.7177	2.5387
1-pentanol	109.145	87.680	21.466	0.5581	76.924	1.7028	2.7138
1-hexanol	125.830	102.399	23.431	0.5445	86.065	1.7370	2.8476

Table 3. Volume Fraction, ϕ_1, of 1,3-Dichlorobenzene, Density, ρ, Speed of Sound, u, Isentropic Compressibility, k_s, and Deviation in Isentropic Compressibility (δK_s) of 1,3-Dichlorobenzene (1) + Methyl Ethyl Ketone (2) 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
0.0581	0.823 38	1175	880	−17
0.1066	0.847 30	1180	848	−29
0.2165	0.901 20	1185	790	−41
0.3071	0.945 27	1190	747	−47
0.4132	0.996 63	1195	702	−48
0.5388	1.057 23	1204	652	−45
0.6322	1.102 23	1210	620	−39
0.7350	1.151 72	1217	586	−30
0.8367	1.200 52	1225	555	−19
0.9728	1.264 69	1240	514	−3
1.0000	1.277 18	1244	506	0

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Table 4. Values of the Parameters b_0, b_1, and b_2 and the Standard Deviation, ΔK_s, for the Binary Systems at 303.15 K

system	b_0/ TPa^{-1}	b_1/ TPa^{-1}	b_2/ TPa^{-1}	(ΔK_s)/ TPa^{-1}
1,3-dichlorobenzene + methyl ethyl ketone	−185.1	103.2	−40.2	2
1,3-dichlorobenzene + 1-propanol	−53.9	33.9	−5.3	1
1,3-dichlorobenzene + 1-butanol	−83.5	73.0	73.0	1
1,3-dichlorobenzene + 1-pentanol	−62.6	56.5	34.3	1
1,3-dichlorobenzene + 1-hexanol	−50.4	57.1	59.4	2

the collision factor theory of Schaaffs. The surface area (Y) and collision factor (S) of pure components, used in the FLT and CFT theories, were calculated using experimental speeds of sound and densities. The remaining parameters, critical temperature (T_c) and surface tension (σ), were taken from the literature (Riddick and Bunger, 1970; Dean, 1987). The values of the molar volume (V), molar volume at absolute zero (V_0), available volume (V_a), free length (L_f), Y, S, and molecular radius (r_m) of the pure components required to predict speed of sound data in terms of the aforesaid theories are given in Table 2. These parameters are calculated using the standard procedure described by Venkatesu et al. (1993).

Experimental and predicted speed of sound data for the four ternary mixtures are given in colums 3−5 of Table 5. The results in the table point out that both theories give a rough estimate of the measured property. However, speeds of sound predicted by CFT are closer to the experimental values.

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

$$k_{s123} = u^{-2}\rho^{-1} \qquad (1)$$

where u and ρ denote the speed of sound and density, respectively. The density was evaluated from measured excess volumes.

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

$$K_{s123} = k_{s123} - k_{s123}^{id} \qquad (2)$$

where k_{s123} and k_{s123}^{id} denote the isentropic compressibilities of the real and ideal mixtures and have the same significance as described earlier (Sivakumar and Naidu, 1994).

The experimental isentropic compressibility, k_{s123}, and deviation in isentropic compressibility, K_{s123}, for four ternary mixtures are given in columns 7 and 8 of Table 5. K_{s123} is negative over the entire volume fraction range.

Table 5. Experimental and Predicted Speed of Sound Data and the Isentropic Compressibility Data for the Ternary Mixtures 1,3-Dichlorobenzene (1) + Methyl Ethyl Ketone (2) + 1-Alkanol (3) at 303.15 K

x_1	x_2	u_{exp}/(m·s^{-1})	u_{FLT}/(m·s^{-1})	u_{CFT}/(m·s^{-1})	ρ/(g·cm^{-3})	k_{s123}/TPa^{-1}	K_{s123}/TPa^{-1}	K_{s123}(bc)/TPa^{-1}	dK_{s123}/TPa^{-1}
			1,3-Dichlorobenzene (1) + Methyl Ethyl Ketone (2) + 1-Propanol (3)						
0.1589	0.1157	1204	1178	1210	0.902 59	764	−42	−15	−27
0.1350	0.1781	1201	1177	1206	0.886 99	782	−39	−15	−24
0.1303	0.2420	1200	1175	1204	0.882 55	787	−39	−16	−23
0.1296	0.3214	1198	1174	1201	0.880 93	791	−40	−18	−22
0.1241	0.4408	1192	1171	1197	0.875 95	803	−36	−20	−16
0.1299	0.5092	1190	1169	1196	0.878 43	804	−35	−23	−12
0.1285	0.5744	1189	1168	1193	0.876 67	807	−36	−25	−11
0.1291	0.7177	1185	1165	1189	0.874 96	814	−35	−30	−5
0.1271	0.8075	1184	1164	1185	0.872 47	818	−36	−34	−2
0.0728	0.8673	1181	1165	1179	0.840 02	854	−27	−23	−4
			1,3-Dichlorobenzene (1) + Methyl Ethyl Ketone (2) + 1-Butanol (3)						
0.1760	0.1385	1220	1203	1228	0.902 68	744	−28	−19	−9
0.1416	0.2269	1217	1200	1221	0.883 01	765	−28	−18	−10
0.1356	0.2765	1214	1197	1218	0.879 21	772	−28	−18	−10
0.1319	0.3731	1207	1192	1212	0.876 59	783	−27	−20	−7
0.1271	0.4926	1201	1185	1205	0.873 32	794	−28	−22	−6
0.1312	0.5683	1198	1180	1201	0.875 43	796	−31	−24	−7
0.1389	0.6359	1197	1175	1197	0.879 64	793	−37	−28	−9
0.1264	0.7008	1193	1172	1193	0.872 18	806	−35	−28	−7
0.1342	0.7548	1190	1169	1190	0.876 43	805	−38	−32	−6
0.0997	0.8407	1184	1166	1183	0.855 94	833	−31	−28	−3
			1,3-Dichlorobenzene (1) + Methyl Ethyl Ketone (2) + 1-Pentanol (3)						
0.2027	0.1371	1240	1226	1246	0.908 92	716	−22	−16	−6
0.1622	0.2488	1232	1219	1237	0.889 22	741	−22	−16	−6
0.1469	0.3176	1227	1214	1231	0.881 67	753	−23	−16	−7
0.1488	0.4168	1221	1204	1223	0.883 16	759	−28	−19	−9
0.1378	0.5365	1209	1194	1213	0.877 75	779	−27	−21	−6
0.1493	0.5747	1205	1189	1210	0.884 26	779	−28	−24	−4
0.1514	0.6579	1196	1180	1202	0.885 77	789	−29	−28	−1
0.1464	0.7579	1189	1171	1193	0.882 98	801	−32	−33	+1
0.0958	0.8539	1183	1168	1184	0.853 51	837	−27	−27	0
0.0672	0.9029	1180	1167	1179	0.836 31	859	−23	−22	−1
			1,3-Dichlorobenzene (1) + Methyl Ethyl Ketone (2) + 1-Hexanol (3)						
0.2476	0.0790	1261	1252	1268	0.922 48	682	−17	−13	−4
0.2158	0.2037	1254	1240	1256	0.909 59	699	−23	−15	−8
0.1866	0.2380	1254	1239	1254	0.896 13	710	−23	−14	−9
0.1621	0.3148	1247	1232	1246	0.885 12	726	−24	−14	−10
0.1534	0.4449	1233	1217	1232	0.882 10	746	−26	−17	−9
0.1537	0.5424	1223	1204	1221	0.883 44	757	−30	−21	−9
0.1562	0.5906	1211	1197	1216	0.885 40	770	−25	−23	−2
0.1543	0.6612	1202	1188	1208	0.885 33	782	−26	−27	+1
0.1229	0.7811	1187	1176	1194	0.868 66	817	−22	−28	+6
0.0789	0.8830	1182	1169	1183	0.843 56	848	−24	−24	0

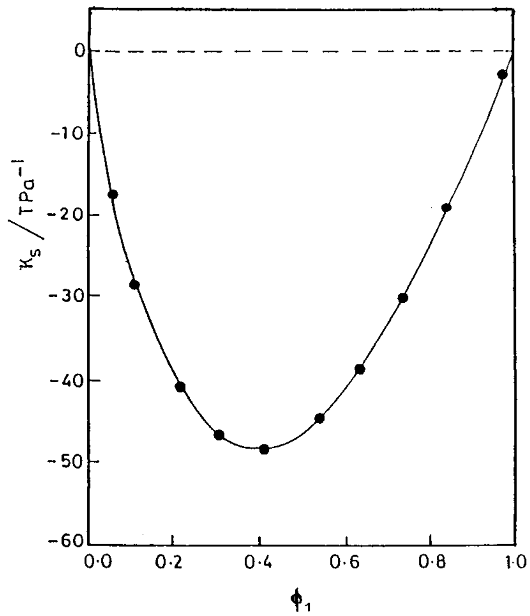

Figure 1. Deviation in isentropic compressibility (K_s) plotted against the volume fraction (ϕ_1) of 1,3-dichlorobenzene with methyl ethyl ketone at 303.15 K.

The deviation in isentropic compressibility, K_{s123} (bc) (bc = binary contribution in the ternary system), for ternary mixtures was computed from the binary data using the relation

$$K_{s123}\text{ (bc)} = K_{s12} + K_{s13} + K_{s23} \qquad (3)$$

where K_{s12}, K_{s13}, and K_{s23} denote deviations in isentropic compressibilities of the constituent binary mixtures. The binary contributions were calculated using the smoothing equation

$$K_{sij} = \phi_i\phi_j[b_0 + b_1(\phi_i - \phi_j) + b_2(\phi_i - \phi_j)^2] \qquad (4)$$

The binary parameters appearing in the above equation (4) for mixtures of 1,3-dichlorobenzene with 1-alkanols were taken from the literature (Chandrakumar and Naidu, 1993; Vijayalakshmi and Naidu, 1995). The binary parameters of mixtures of 1,3-dichlorobenzene with methyl ethyl ketone were also estimated. These values are presented in Table 3 and are graphically represented in Figure 1. The binary parameters for all the above mixtures are listed in Table 4 along with the standard deviations. Binary parameters for the mixtures of methyl ethyl ketone with 1-alkanols (Reddy & Naidu, 1978) at 303.15 K were taken to be close to zero as the deviation in isentropic compressibility was close to experimental error. Hence, K_{s23} has been ignored in the calculation of K_{s123} (bc) in eq 3.

The values of K_{s123} (bc), computed from constituent binary data, are reported in column 9 of Table 5. The differences between K_{s123} and K_{s123} (bc) (denoted by dK_{s123}) are given in column 10 of Table 5.

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