Speed of Sound and Isentropic Compressibilities of Ternary Mixtures Containing *p*-Chlorotoluene, Hexane, and 1-Alkanols at 303.15 K

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Isentropic compressibilities of three ternary mixtures *p*-chlorotoluene + hexane + 1-pentanol, and + 1-hexanol, and + 1-heptanol were determined from speed of sound measurements at 303.15 K. The deviations in the isentropic compressibility were also computed. The deviations exhibit an inversion in sign.

Introduction

This work forms part of a study of thermodynamic properties of ternary mixtures (*1*). Thermodynamic properties of pure liquids and liquid mixtures are of interest both to chemists and to chemical engineers for processing of petroleum and petrochemical products. The present study was undertaken to determine the isentropic compressibilitity from speed of sound measurements and the density evaluated from excess volumes. Further, the third component brings a change in both the nature and degree of interaction between pairs of molecules. We present here experimental data for the isentropic compressibility of three ternary mixtures, *p*-chlorotoluene + hexane + 1-pentanol, + 1-hexanol, and + 1-heptanol.

Experimental Section

Apparatus and Procedure. Isentropic compressibilities were computed from the measured speed of sound and the density, evaluated from excess volume measurements. Excess volumes as a function of composition were measured directly by a dilatometric method described earlier (*2*). The speed of sound was measured with a single-crystal interferometer at a frequency of 4 MHz, and the values are accurate to ±0.015%. All the measurements were made at a constant temperature employing a thermostat that could maintain the temperature of 303.15 ± 0.01 K. Isentropic compressibilities calculated from the speed of sound and density are accurate to ±2 TPa^{-1}.

Materials. All the chemicals used were of analytical grade. *p*-Chlorotoluene was purified by the method described by Vogel (*3*). Alkanols and hexane were purified by the methods described by Riddick and Bunger (*4*). *p*-Chlorotoluene (Fluka) was washed successively with an aqueous 10% solution of sodium hydroxide, concentrated sulfuric acid, and water. It was dried with anhydrous calcium chloride, decanted, and distilled. 1-Pentanol (Fluka) and 1-hexanol (Merck) were dried over Drierite and fractionally distilled. 1-Heptanol (S.D. Fine Chemicals) was fractionally distilled. Hexane (BDH) was shaken several times with concentrated sulfuric acid, then with a 0.1 M solution of potassium permanganate in 10% sulfuric acid, and finally with a 0.1 M solution of permanganate in 10% sodium hydroxide. The sample was washed with water, dried over sodium wire, and distilled.

The purities of the samples were checked by comparing the measured densities of the components with those reported in the literature (*5*, *6*). The densities of pure liquids were measured with a bicapillary pycnometer which offered an accuracy of ±0.000 02 g cm^{-3}. The measured densities and those reported in the literature are presented in Table I.

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Table I. Densities, ρ, of Pure Liquids at 303.15 K

component	ρ/(g cm^{-3}) this work	ρ/(g cm^{-3}) lit. (*5*, *6*)
p-chlorotoluene	1.065 14[a]	1.06 510[a]
1-pentanol	0.807 62	0.80 764
1-hexanol	0.812 05	0.81 201
1-heptanol	0.815 72	0.81 574
n-hexane	0.650 63	0.65 070

[a] At 298.15 K.

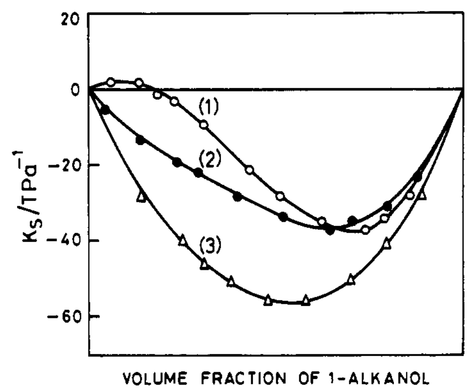

Figure 1. Deviation in isentropic compressibilities K_s at 303.15 K plotted against the volume fraction ϕ_1 for hexane (1) + 1-pentanol (2), hexane (1) + 1-hexanol (2), and hexane (1) + 1-heptanol (2), labeled 1, 2, and 3, respectively.

Results and Discussion

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

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

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

The densities for ternary mixtures were calculated from the relation

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

where x_1, x_2, and x_3 and M_1, M_2, and M_3 denote the mole fractions and molecular weights of *p*-chlorotoluene, 1-alkanol, and hexane, respectively. $V = \epsilon x_i V_i^\circ$ where V_i° is the molar volume of pure component i and V^{E}_{123} is the experimental excess molar volume.

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Table II. Experimental Values for Isentropic Compressibilities of Ternary Systems: *p*-Chlorotoluene (1) + 1-Alkanol (2) + Hexane (3) at 303.15 K

ϕ_1	ϕ_2	ρ/ (g cm^{-3})	u/ (m s^{-1})	k_{s123}/ TPa^{-1}	K_{s123}/ TPa^{-1}	K'_{s123}/ TPa^{-1}	dK_{s123}/ TPa^{-1}
		p-Chlorotoluene (1) + 1-Pentanol (2) + Hexane (3)					
0.1655	0.1625	0.745 26	1121	1067	−89	−71	−18
0.1805	0.2016	0.757 62	1131	1032	−88	−71	−17
0.1430	0.2345	0.747 46	1122	1062	−68	−61	−7
0.1253	0.2975	0.749 90	1127	1050	−56	−56	0
0.1859	0.3586	0.784 68	1149	965	−56	−62	6
0.2142	0.4568	0.812 01	1171	898	−40	−59	19
0.1628	0.3198	0.800 63	1172	909	−33	−54	21
0.1885	0.5812	0.820 90	1193	856	−28	−50	22
0.1970	0.6486	0.834 70	1218	807	−29	−43	14
0.2091	0.6744	0.843 75	1230	783	−27	−38	11
		p-Chlorotoluene (1) + 1-Hexanol (2) + Hexane (3)					
0.1576	0.2361	0.755 14	1125	1046	−62	−80	18
0.1761	0.1992	0.756 85	1129	1036	−81	−97	16
0.2342	0.1506	0.773 15	1120	1031	−71	−86	15
0.1619	0.3009	0.767 42	1137	1008	−55	−73	18
0.1696	0.4461	0.794 07	1171	919	−44	−54	10
0.1553	0.5490	0.804 80	1198	865	−43	−41	−2
0.1880	0.5951	0.825 68	1226	806	−46	−33	−13
0.1857	0.6050	0.826 31	1228	802	−45	−32	−13
0.1860	0.6088	0.827 07	1230	799	−46	−31	−15
0.1264	0.7527	0.825 24	1251	774	−26	−16	−10
		p-Chlorotoluene (1) + 1-Heptanol (2) + Hexane (3)					
0.1942	0.1743	0.760 90	1126	1037	−77	−95	18
0.2097	0.2170	0.774 23	1139	996	−76	−93	17
0.1392	0.2710	0.754 56	1142	1016	−77	−82	5
0.1375	0.3240	0.762 70	1155	983	−75	−79	4
0.1287	0.4098	0.773 38	1176	935	−73	−72	−1
0.1746	0.5797	0.820 72	1235	799	−57	−53	−4
0.1598	0.6145	0.82− 31	1242	790	−54	−49	−5
0.1798	0.6636	0.836 80	1258	755	−40	−38	−1
0.1167	0.7479	0.823 95	1267	756	−33	−32	−1
0.0962	0.7704	0.818 98	1271	756	−34	−33	−1

The deviation in isentropic compressibility, K_{s123}, for a ternary mixture was computed employing the relation

$$K_{s123} = k_{s123} - k_{s123}^{\mathrm{id}} \tag{3}$$

where k_{s123} and k_{s123}^{id} are isentropic compressibilities of the real and an ideal mixture, respectively. The ideal isentropic compressibility was assumed to be additive in terms of volume fraction and was calculated using the relation

$$k_{s123}^{\mathrm{id}} = \phi_1 k_{s1} + \phi_2 k_{s2} + \phi_3 k_{s3} \tag{4}$$

where ϕ_1, ϕ_2, and ϕ_3 and k_{s1}, k_{s2}, and k_{s3} are volume fractions and isentropic compressibilities of *p*-chlorotoluene, an alkanol, and hexane, respectively.

The quantity dK_{s123}, the difference between the measured value and that computed from constituent binary data, was calculated as shown below:

$$\mathrm{d}K_{s123} = K_{s123} - K'_{s123} \tag{5}$$

where K_{s123} is the deviation in isentropic compressibility calculated from experimental data and K'_{s123} is the deviation calculated from binary data. The latter quantity was calculated using the relation

$$K'_{s123} = K_{s12} + K_{s13} + K_{s23} \tag{6}$$

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

$$K_{sij} = \phi_i\phi_j[a_0 + a_1(\phi_i - \phi_j) + a_2(\phi_i - \phi_j)^2] \tag{7}$$

where a_0, a_1, and a_2 are constants obtained by the method of least squares.

Further, the binary parameters for the deviation in isentropic compressibility to compute ternary data for mixtures of *p*-chlorotoluene with 1-alkanols, *p*-chlorotoluene with hexane, and hexane with 1-alkanols were taken from the literature (7–9). These parameters are given in Table III along with the standard deviation $\sigma(K_s)$. Also the deviation in isentropic compressibility data for mixtures of hexane with 1-alkanols is graphically presented in Figure 1.

Table III. Values of the Parameters a_0, a_1, and a_2 and the Standard Deviation $\sigma(K_s)$ for Binary Systems at 303.15 K

system	a_0/ TPa^{-1}	a_1/ TPa^{-1}	a_2/ TPa^{-1}	$\sigma(K_s)$/ TPa^{-1}
p-chlorotoluene + 1-pentanol	−23.0	103.5	−23.8	1
p-chlorotoluene + 1-hexanol	6.4	66.4	−2.5	1
p-chlorotoluene + 1-heptanol	26.2	53.3	−20.6	1
p-chlorotoluene + hexane	−454.9	199.0	−229.6	2
1-pentanol + hexane	−109.6	−172.3	3.0	2
1-hexanol + hexane	−128.8	74.5	−59.0	1
1-heptanol + hexane	−214.4	−26.2	−48.6	1

Table IV. Values of Ternary Constants *A*, *B*, and *C* and the Standard Deviation $\sigma(\mathrm{d}K_{s123})$ of Ternary Systems at 303.15 K

system	*A*/ TPa^{-1}	*B*/ TPa^{-1}	*C*/ TPa^{-1}	$\sigma(\mathrm{d}K_{s123})$/ TPa^{-1}
p-chlorotoluene (1) + 1-pentanol (2) + hexane (3)	447	10 523	−75 034	1
p-chlorotoluene (1) + 1-hexanol (2) + hexane (3)	435	−9 544	−67 350	2
p-chlorotoluene (1) + 1-heptanol (2) + hexane (3)	−60	−5 119	55 937	2

The experimental isentropic compressibility, k_{s123}, and the deviation in isentropic compressibility, K_{s123}, for the ternary mixtures are given in columns 5 and 6 of Table II. Finally, the quantity dK_{s123} is given in column 8 of Table II.

An examination of results included in Table II shows that the values of dK_{s123} are nonzero. This suggests that the ternary mixtures are not ideal in terms of constituent binaries. This shows that the third component modifies both the nature and degree of interaction between molecules of components. The algebraic values of dK_{s123} fall in the order 1-pentanol > 1-hexanol ≈ 1-heptanol. This shows that there is no simple correlation between the chain length of alkanols and dK_{s123}.

The dK_{s123} values were fitted to the polynomial

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

where ϕ_1, ϕ_2, and ϕ_3 are the volume fractions of components 1, 2, and 3, respectively. The values of adjustable parameters *A*, *B*, and *C* are obtained by the least-squares method and are given in Table IV along with the standard deviations $\sigma(\mathrm{d}K_{s123})$.

Glossary

k_{s123}	isentropic compressibility of a ternary mixture, eq 1
K_{s123}	deviation in isentropic compressibility of a ternary mixture, eq 3
K'_{s123}	deviation in isentropic compressibility for the ternary system computed from the binary data, eq 6
dK_{s123}	difference between K_{s123} and K'_{s123}, eq 5
ϕ	volume fraction
K_{sij}	deviation in isentropic compressibility of any two components in a ternary mixture
a_0,a_1,a_2	binary constants in eq 7
A,*B*,*C*	ternary constants in eq 8

Subscripts

1,2,3	components

Superscripts

E	excess property

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