Speed of Sound and Isentropic Compressibilities of Trichloroethylene with Branched Alcohols at 303.15 K

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The speed of sound for the binary mixtures of trichloroethylene with branched alcohols has been determined at 303.15 K. The branched alcohols include 2-propanol, 2-methyl-1-propanol, 3-methyl-1-butanol, 2-butanol, and 2-methyl-2-propanol. Further, isentropic compressibilities (K_s) and deviation in isentropic compressibilities (ΔK_s) have been computed from the sound velocity and density data derived from excess volumes. The results show that ΔK_s values are positive over the entire range of composition for the systems trichloroethylene + 3-methyl-1-butanol, + 2-butanol, and + 2-methyl-2-propanol, and an inversion of sign from negative to positive is observed for the remaining systems trichloroethylene + 2-propanol and + 2 methyl-1-propanol.

Introduction

Sound velocities and its related properties have been used to study physicochemical behavior and molecular interactions in a variety of liquid mixtures (Venkatesulu and Rao 1992; Venkatesu et al., 1993, 1995). A survey of literature has shown that there are few measurements on the sound velocity and isentropic compressibility of binary mixtures of branched alcohols with trichloroethylene. Hence we present here speed of sound and isentropic compressibilities of trichloroethylene with 2-propanol, 2-methyl-1-propanol, 3-methyl-1-butanol, 2-butanol, and 2-methyl-2-propanol at 303.15 K.

Experimental Section

Materials. All the chemicals used were of analytical grade. Trichloroethylene (Merck) was purifed by the method described by Nath et al. (1989). The branched alcohols (Fluka) were further purified by the methods described by Babu et al. (1989). The purity of the chemicals was checked by comparing the measured densities with those reported in literature (Ramanjaneyulu et al., 1989; Babu et al., 1989). The densities of all components were measured by a bicapillary pycnometer and are accurate to 2 parts in 10^5. The measured densities, speed of sound, and the literature data are presented in Table 1.

Apparatus. Isentropic compressibilities were computed from the measured speed of sound and densities evaluated from excess volumes (Venkatesulu et al., 1997). The speeds of sound for the title systems were measured with a single-crystal interferometer at a frequency of 4 MHz at 303.15 K and were accurate to ±0.02%. All the measurements were made at a constant temperature employing a thermostat that could be maintained at ±0.01 K.

Results and Discussion

Isentropic compressibilities (K_s) of the binary mixtures were calculated from the relation

$$K_s = U^{-2}\rho^{-1} \quad (1)$$

The deviation in isentropic compressibility (ΔK_s) were evaluated from the equation

Table 1. Speed of Sound (U) and Densities (ρ) of Pure Components at 303.15 K

components	U/m s^{-1} exptl	U/m s^{-1} lit	ρ/g cm^{-3} exptl	ρ/g cm^{-3} lit
trichloroethylene	1014	1013[a]	1.451 34	1.451 36[c]
2-propanol	1126	1127[b]	0.776 86	0.776 90[b]
2-methyl-1-propanol	1172	1172[b]	0.794 34	0.794 37[b]
3-methyl-1-butanol	1220	1220[b]	0.801 74	0.801 79[b]
2-butanol	1194	1195[b]	0.798 91	0.798 95[b]
2-methyl-2-propanol	1104	1105[b]	0.776 16	0.776 20[b]

[a] Nath et al., 1989. [b] Babu et al., 1989. [c] Ramanjaneyulu et al., 1989.

$$\Delta K_s = K_s - \phi_1 K_{s1} - \phi_2 K_{s2} \quad (2)$$

where ϕ_1 and ϕ_2 are volume fractions of the components and K_s, K_{s1}, and K_{s2} are the isentropic compressibilities of the mixture and the pure components, respectively.

The experimental data for five binary mixtures are presented in Table 2. The dependence of ΔK_s on volume fraction of trichloroethylene was shown in Figure 1. The ΔK_s values may be fitted to an empirical equation of the form

$$\Delta K_s = \phi_1\phi_2[b_0 + b_1(\phi_1 - \phi_2) + b_2(\phi_1 - \phi_2)^2] \quad (3)$$

The values of the parameters b_0, b_1, and b_2 computed by the method of least squares are given in Table 3 along with standard deviation (σ), which is evaluated from the equation

$$\sigma = \left[\frac{\sum(\Delta K_{s\,exp} - \Delta K_{s\,cal})^2}{n - p}\right]^{1/2} \quad (4)$$

where n and p are number of results and number of parameters, respectively. The ΔK_s values are accurate to ±2 TPa^{-1}.

The results included in Table 2 show that ΔK_s values are positive over the entire range of composition for the systems trichloroethylene with 3-methyl-1-butanol, 2-butanol, and 2-methyl-2-propanol, and a change of sign from negative to positive is observed for the remaining systems trichloroethylene + 2-propanol and + 2-methyl-1-propanol. The ΔK_s values may be attributed to (i) an increase in free spaces in mixtures compared to those in pure components due to the depolymerization of alcohol aggregates with the

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Table 2. Volume Fraction (ϕ_1) of Trichloroethylene, Density (ρ), Speed of Sound (U), Isentropic Compressibility (K_s), and Deviation in Isentropic Compressibility (ΔK_s) for the Binary Mixtures of Trichloroethylene with Branched Alcohols at 303.15 K.

ϕ_1	ρ/g cm^{-3}	U_{exp}/m s^{-1}	K_s/TPa^{-1}	ΔK_s/TPa^{-1}
Trichloroethylene (1) + 2-Propanol (2)				
0.0000	0.776 86	1126.0	1015.3	
0.1191	0.856 91	1103.2	958.9	−15.4
0.2486	0.943 68	1081.2	906.5	−23.1
0.3795	1.031 24	1058.8	865.0	−19.5
0.4559	1.082 36	1045.6	845.1	−13.1
0.5524	1.147 02	1029.2	823.1	−1.8
0.6394	1.205 39	1018.0	800.5	5.5
0.7502	1.280 12	1008.0	768.8	12.0
0.8255	1.331 25	1004.8	744.0	13.2
0.9158	1.393 02	1006.0	709.3	9.6
1.0000	1.451 34	1013.6	670.7	
Trichloroethylene (1) + 2-Methyl-1-propanol (2)				
0.0000	0.794 34	1172.0	916.5	
0.1057	0.864 08	1141.6	888.0	−2.5
0.2077	0.931 12	1116.0	862.3	−3.1
0.3113	0.998 96	1089.6	843.2	3.2
0.3946	1.053 31	1071.2	827.4	7.9
0.5103	1.128 67	1048.8	805.5	14.4
0.5970	1.185 11	1035.2	787.4	17.6
0.7130	1.260 80	1020.8	761.2	20.0
0.8081	1.323 22	1012.8	736.8	18.9
0.9120	1.392 13	1008.8	705.8	13.5
1.0000	1.451 34	1013.6	670.7	
Trichloroethylene (1) + 3-Methyl-1-butanol (2)				
0.0000	0.801 74	1220.0	838.0	
0.0771	0.851 23	1189.6	829.3	4.2
0.1735	0.914 91	1156.0	817.9	8.9
0.2360	0.955 51	1136.8	809.8	11.3
0.3663	1.039 80	1100.0	794.8	18.1
0.4569	1.098 34	1078.4	782.9	21.3
0.5741	1.173 92	1054.4	766.2	24.2
0.6594	1.229 01	1039.2	753.4	25.7
0.7828	1.308 96	1022.4	730.9	23.9
0.8866	1.376 65	1012.8	708.2	18.5
1.0000	1.451 34	1013.6	670.7	
Trichloroethylene (1) + 2-Butanol (2)				
0.0000	0.798 91	1194.4	877.4	
0.1080	0.868 88	1157.6	858.9	3.8
0.2089	0.934 07	1126.8	843.2	9.0
0.3068	0.997 17	1101.6	826.4	12.4
0.4027	1.058 98	1079.6	810.2	16.0
0.5157	1.131 86	1056.8	791.1	20.3
0.6074	1.191 20	1040.8	775.0	23.1
0.7043	1.254 31	1027.2	755.6	23.8
0.8087	1.326 45	1015.2	731.5	21.3
0.8990	1.382 98	1010.4	708.3	16.7
1.0000	1.451 34	1013.6	670.7	
Trichloroethylene (1) + 2-Methyl-2-propanol (2)				
0.0000	0.776 16	1104.0	1057.1	
0.0993	0.841 56	1078.8	1021.0	2.3
0.2016	0.909 41	1057.2	983.8	4.6
0.3050	0.978 37	1039.2	946.5	7.3
0.4014	1.042 83	1025.6	911.7	9.7
0.5014	1.109 70	1014.0	876.4	13.0
0.6078	1.181 00	1005.6	837.3	15.1
0.6991	1.242 49	1000.4	804.2	17.2
0.7951	1.293 45	1004.8	765.7	15.8
0.9043	1.383 20	1002.4	719.5	11.8
1.0000	1.451 34	1013.6	670.7	

addition of trichloroethylene and (ii) a decrease in free spaces as a result of weak hydrogen-bonding interactions of the type C1··· H−O between unlike molecules and interstitial accommodation of trichloroethylene in hydrogen-bonded aggregates of alcohols. The former factor leads to positive ΔK_s values, and the latter effect contributes to negative values of ΔK_s. The actual deviation in isentropic compressibility would be the resultant of the aforesaid effects. The algebraic values of ΔK_s at equimolar mixtures fall in the order

3-methyl-1-butanol > 2-butanol > 2-methyl-1-propanol > 2-methyl-2-propanol > 2-propanol

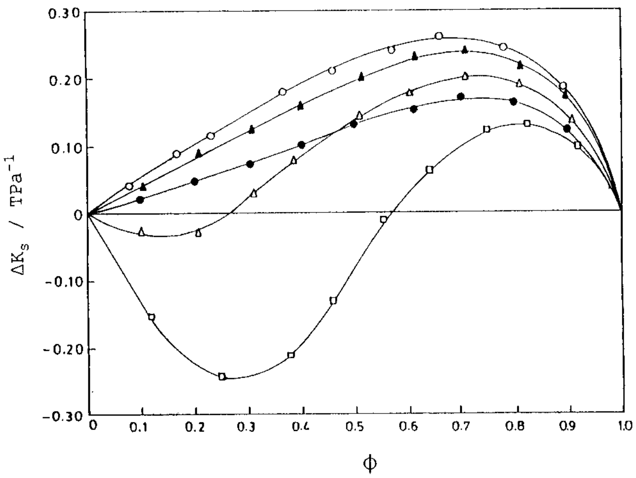

Figure 1. Deviation in isentropic compressibilities (ΔK_s) as a function of volume fraction (ϕ) for trichloroethylene + 2-methyl-2-propanol (●), + 2-butanol (▲), + 2-propanol (□), + 2-methyl-1-propanol (△), and + 3-methyl-1-butanol (○) at 303.15 K.

Table 3. Least-Squares Parameters of Equation 3 and Standard Deviation (σ) for the Mixtures of Trichloroethylene (1) + Branched Alcohols (2) at 303.15 K

trichloroethylene (1) +	b_0[a]	b_1[a]	b_2[a]	$\sigma(\Delta K_s)$[a]
2-propanol (2)	−33.41	176.71	23.28	1.5
2-methyl-1-propanol (2)	50.93	115.86	20.23	1.3
3-methyl-1-butanol (2)	88.86	75.20	50.77	0.9
2-butanol (2)	78.02	80.15	50.89	1.0
2-methyl-2-propanol (2)	49.75	63.71	45.85	0.6

[a] In TPa^{-1}.

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