Ultrasonic Studies for Binary Mixtures with Trichloroethylene + Alkan-1-ols (C₃−C₈) at 303.15 K

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Sound velocity for trichloroethylene + propan-1-ol, + butan-1-ol, + pentan-1-ol, + hexan-1-ol,+ heptan-1-ol, and + octan-1-ol have been measured at 303.15 K. These results have been combined with our previous results for excess molar volumes converted to densities to obtain isentropic compressibilities, k_s. Deviations in the isentropic compressibility properties, Δk_s, were evaluated using volume fraction weighing of the individual component properties to estimate ideal mixture behavior. The Δk_s values are negative over the whole range of volume fraction for all the mixtures and at the minimum decreases with an increase in chain length of the alcohol. For all systems, these results were satisfactorily correlated by the Redlich−Kister polynomial. The results are explained in terms of dissociation of the self-associated alkan-1-ol molecules and the formation of aggregates between unlike molecules through Cl···H···O bonding.

Introduction

The acoustic properties of binary liquid mixtures can be quite significant and give a measure of molecular interactions and, hence, can provide information needed to test existing theories of solutions.

This paper forms part of a series on the measurement of thermodynamic and acoustic properties of nonelectrolyte solutions for binary mixtures with trichloroethylene and tetrachloroethylene as a component in which specific interactions between unlike molecules can occur (Iloukhani et al., 1984; Iloukhani and Rao, 1985; Iloukhani, 1997; Iloukhani and Parsa, 1998; Iloukhani and Ghorbani, 1998). Sound velocities, u, isentropic compressibilities, k_s, and deviations in the isentropic compressibilities, Δk_s for trichloroethylene + propan-1-ol, + butan-1-ol, + pentan-1-ol, + hexan-1-ol, + heptan-1-ol, and + octan-1-ol at 303.15 K are reported.

Experimental Section

Materials. The materials used in this study, suppliers, and their purities are listed in Table 1. Trichloroethylene was purified by the standard method (Carlisle and Levine, 1932) described by Riddick and Bunger (1970). All alkan-1-ols were purified by the standard method described by (Perrin and Armarego, 1970).

The purities of all the liquid samples were ascertained by the accuracy of their boiling points and also from their density values, which agreed as shown in Table 1 with the literature values (Riddick and Bunger, 1970; Timmermans, 1962). The boiling points at 101.32 kPa were measured using a Swietoslawski type ebulliometer, which gave an accuracy of ±0.2 K. The densities were measured at 303.15 K using a bicapillary pycnometer with an accuracy of 5 parts in 10^5.

Apparatus and Procedure. Mixtures were prepared by weighing the liquids in ground stoppered weighing bottles, taking due precaution to minimize the evaporation losses. All the weightings were performed on an electronic balance (Mettler AE 163, Switzerland) accurate to 0.01 mg.

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Table 1. Source, Purity Grades, Densities, (ρ), and Boiling Points (T_b) of the Pure Components at 303.15 K

component	source	purity/ (mass %)	ρ/g·cm^{-3} expt.	ρ/g·cm^{-3} lit.[a]	T_b/K expt.	T_b/K lit.[a]
trichloroethylene	Merk	99.5	1.451 33	1.451 4	360.1	360.3
propan-1-ol	Fluka	99	0.795 91	0.796 00	370.2	370.3
butan-1-ol	Merk	99	0.802 00	0.802 06	390.7	390.9
pentan-1-ol	Merk	99	0.807 55	0.807 64	411.0	411.2
hexan-1-ol	Fluka	≥99.5	0.811 91	0.812 01	430.9	431.0
heptan-1-ol	Fluka	≥99	0.821 82[b]		448.9	449.1
octan-1-ol	Fluka	≥99.5	0.821 87	0.821 92	467.5	467.6

[a] Riddick and Bunger 1970; Timmermans, 1962. [b] At 293.15 K.

The possible error in the mole fraction is estimated to be lower than $\pm 2 \times 10^{-4}$.

Ultrasonic sound velocities, u, in the pure liquids and the six binary mixtures were measured with a single-crystal multifrequency ultrasonic interferometer. In the present work, a steel cell fitted with a quartz crystal of 1 MHz frequency was employed. In these measurements the temperature was maintained constant by circulating water around a liquid cell from a thermostat controlled at (303.15 ± 0.01) K. The accuracies in the values of the sound velocities, u, and densities, are estimated to be ±1.0 m·s^{-1} and 0.01%, respectively.

Results and Discussion

Sound velocities of trichloroethylene + propan-1-ol, + butan-1-ol, + pentan-1-ol, + hexan-1-ol, + heptan-1-ol, and + octan-1-ol at different mole fractions at 303.15 K are reported in Table 2.

Densities of binary mixtures for the calculations of isentropic compressibilities for six systems were calculated from accurate excess molar volumes V^E (Iloukhani et al., 1984)

$$\rho = \sum_{1}^{2} x_i M_i / (x_i V_i^0 + V^E) \quad (1)$$

where V_i^0 and M_i are the molar volume and molar mass of pure component i.

Table 2. Density (ρ/g·cm^{-3}), Sound Velocity (u/m·s^{-1}), Isentropic Compressibility (k_s/TPa^{-1}), and Deviation in Isentropic Compressibility (Δk_s/TPa^{-1}) for Binary Mixtures of x Trichloroethylene + $(1 - x)$Alkan-1-ols at 303.15 K

x	ϕ	ρ	u	k_s	Δk_s	x	ϕ	ρ	u	k_s	Δk_s
					xC$_2$Cl$_3$H + $(1 - x)$C$_3$H$_7$OH						
0.0000	0.0000	0.795 96	1190	886		0.5319	0.5767	1.182 05	1084	720	−41
0.0915	0.1077	0.867 10	1165	849	−14	0.6277	0.6690	1.239 98	1067	708	−33
0.1902	0.2197	0.940 25	1145	811	−28	0.7314	0.7655	1.301 27	1050	698	−23
0.2616	0.2981	10.005 27	1127	783	−39	0.8007	0.8281	1.342 46	1038	692	−15
0.3319	0.3732	10.043 19	1121	763	−42	0.8715	0.8905	1.382 51	1027	685	−8
0.4516	0.4968	10.130 05	1098	734	−45	1.000	1.000	1.451 34	1014	670	
					xC$_2$Cl$_3$H + $(1 - x)$C$_4$H$_9$OH						
0.0000	0.0000	0.802 01	1223	833		0.5409	0.5358	1.150 50	1110	705	−41
0.1002	0.0983	0.866 21	1201	801	−17	0.6198	0.6049	1.200 71	1093	697	−37
0.1844	0.1813	0.920 45	1183	776	−27	0.7400	0.7360	1.282 84	1060	693	−26
0.2711	0.2670	0.976 48	1165	754	−36	0.8101	0.8069	1.331 38	1049	683	−18
0.3549	0.3502	1.031 45	1151	732	−44	0.8976	0.8956	1.390 20	1028	680	−6
0.4412	0.4361	1.092 51	1125	723	−44	1.000	1.000	1.451 34	1014	670	
					xC$_2$Cl$_3$H + $(1 - x)$C$_5$H$_{11}$OH						
0.0000	0.0000	0.807 55	1257	784		0.5722	0.5259	1.150 27	1122	691	−33
0.1234	0.1045	0.875 20	1228	757	−15	0.6629	0.6199	1.216 63	1097	683	−30
0.2105	0.1811	0.925 07	1209	739	−24	0.7705	0.7357	1.292 18	1070	675	−24
0.3155	0.2765	0.986 66	1183	724	−28	0.8396	0.8127	1.331 94	1056	673	−18
0.3706	0.3281	1.022 12	1168	717	−29	0.9213	0.9066	1.402 22	1032	670	−10
0.4719	0.4256	1.088 18	1145	701	−34	1.000	1.000	1.451 34	1014	670	
					xC$_2$Cl$_3$H + $(1 - x)$C$_6$H$_{13}$OH						
0.0000	0.0000	0.811 95	1285	746		0.5718	0.4899	1.134 20	1133	687	−22
0.1223	0.0911	0.871 02	1255	728	−11	0.6628	0.5857	1.187 40	1112	681	−21
0.2166	0.1659	0.918 14	1235	715	−19	0.7719	0.7088	1.266 94	1080	672	−16
0.3054	0.2403	0.966 23	1210	707	−21	0.8421	0.7932	1.320 04	1059	675	−11
0.3779	0.3041	1.012 01	1188	701	−22	0.9282	0.9029	1.394 49	1033	672	−5
0.4954	0.4139	1.077 29	1160	690	−25	1.000	1.000	1.451 34	1014	670	
					xC$_2$Cl$_3$H + $(1 - x)$C$_7$H$_{15}$OH						
0.0000	0.0000	0.815 72	1310	714		0.5993	0.4877	1.137 58	1144	672	−20
0.1234	0.0822	0.868 21	1276	708	−3	0.6814	0.5765	1.195 19	1117	670	−19
0.2621	0.1844	0.933 10	1240	697	−9	0.7793	0.6921	1.260 06	1090	668	−15
0.3432	0.2496	0.975 29	1217	692	−11	0.8654	0.8036	1.337 99	1057	669	−10
0.4302	0.3246	1.031 73	1189	686	−14	0.9431	0.9135	1.396 42	1035	668	−5
0.5117	0.4002	1.082 94	1167	678	−18	1.000	1.000	1.451 34	1014	670	
					xC$_2$Cl$_3$H + $(1 - x)$C$_8$H$_{17}$OH						
0.0000	0.0000	0.821 88	1331	687		0.5814	0.4424	1.108 88	1165	664	−15
0.1503	0.0918	0.882 83	1289	682	−4	0.6818	0.5504	1.169 75	1134	664	−13
0.2876	0.1874	0.947 76	1248	677	−7	0.7554	0.6382	1.236 15	1103	664	−12
0.3198	0.2117	0.962 04	1242	674	−9	0.8411	0.7534	1.300 73	1075	665	−9
0.3921	0.2692	1.002 39	1218	672	−10	0.9314	0.8858	1.382 88	1041	667	−5
0.4702	0.3364	1.044 57	1197	668	−13	1.000	1.000	1.451 34	1014	670	

The specific compression of solution is defined as the partial derivative of specific volume, V, with respect to pressure, p under isentropic conditions: $k_s = -(\partial V/\partial p)_s$.

Then, the isentropic compressibility, k_s^{id}, values can be estimated from the relation

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

where ρ is the density of the mixture.

Defining the ideal isentropic solution property, k, is not as straightforward as for the ideal molar volumes, V^{id} (Douheret et al., 1992). However, one may write a defining equation in terms of the volume fraction average (Benson and Kiyohara, 1979; Baumgartner and Atkinson, 1971; Masood et al., 1977).

$$k_s^{id} = \sum_i (k_{s,i}^*)\phi_i \qquad (3)$$

where $k_{s,i}^*$ is the isentropic compressibility of pure component i, and $\phi_i = x_i V_i^0/\sum x_j V_j$ is volume fraction of component i. Then the deviations in isentropic compressibility, Δk_s from the ideal mixing values can be estimated from the following equation

$$\Delta k_s = k_s - \sum_i (k_{s,i}^*)\phi_i \qquad (4)$$

The values of k_s and Δk_s are also recorded in Table 2. Dependence of Δk_s and k_s on volume fraction and composition, respectively, are shown in Figures 1 and 2. The isentropic compressibilities, k_s, and deviations in isentropic compressibilities, Δk_s, values are believed to be reliable to within 1.0 TPa.

The Δk_s values were correlated with the composition data by means of the Redlich−Kister polynomial (1948), which for binary mixtures is

$$\Delta k_s = \phi (1 - \phi)\sum_{k=0} a_k (1 - 2\phi)^k \qquad (5)$$

where ϕ is the volume fraction of trichloroethylene, a_k is the polynomial coefficient, and k is the number of the polynomial coefficient.

In each case, the optimum number of the polynomial coefficient was ascertained from an examination of the variation of the standard deviation, $\sigma(\Delta k_s)$, with

$$\sigma(\Delta k_s) = [\sum (k_{s(\exp t)} - k_{s(calcd)})^2/(n - p)]^{1/2} \qquad (6)$$

where n and p are the number of results and number of
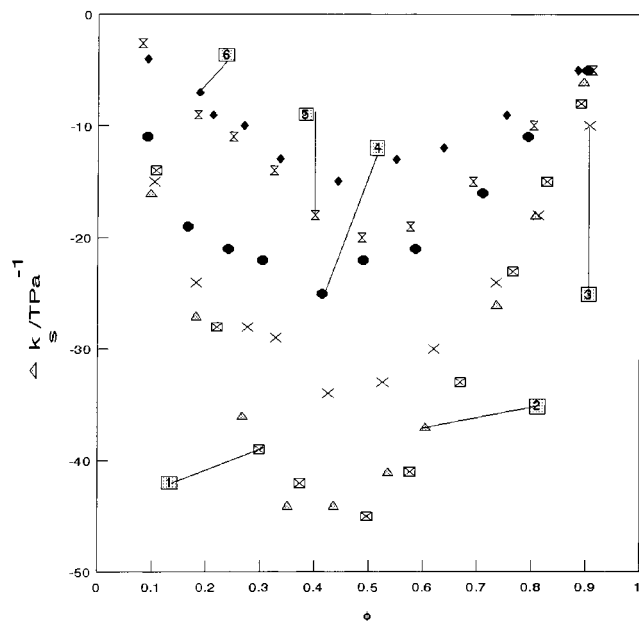
Figure 1. Dependence of deviation in isentropic compressibility on volume fraction of trichloroethylene at 303.15 K for mixtures of trichloroethylene with alkan-1-ols. Experimental points: 1, propan-1-ol; 2, butan-1-ol; 3, pentan-1-ol; 4, hexan-1-ol; 5, heptan-1-ol; 6, octan-1-ol.
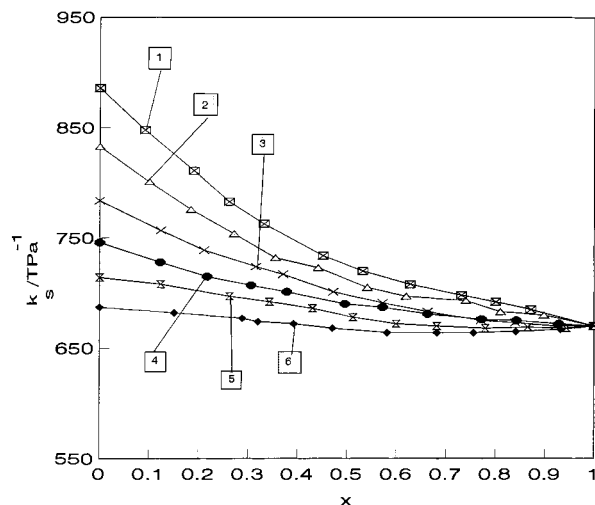
Figure 2. Dependence of isentropic compressibility on mole fraction of trichloroethylene at 303.15 K for mixtures of trichloroethylene with alkan-1-ols. Experimental points: 1, propan-1-ol; 2, butan-1-ol; 3, pentan-1-ol; 4, hexan-1-ol; 5, heptan-1-ol; 6, octan-1-ol.

adjustable parameters, a_k, retained in eq 5, respectively. The values adopted for the polynomial coefficient, a_k, and the standard deviation, $\sigma(\Delta k_s)$, estimates associated with the use of eq 5 and eq 6, respectively, are summarized in Table 3.

Table 3. Polynomial Coefficient, a_k, in Eq 5, and Standard Deviation, $\sigma(\Delta k_s)$, in Eq 6, for xTrichloroethylene + (1 − x)Alkan-1-ols at 303.15 K

system	TPa^{-1}			
	a_0	a_1	a_2	$\sigma(\Delta k_s)$
xC$_2$Cl$_3$H + (1 − x)C$_3$H$_7$OH	−184.6909	45.9726	126.3404	1
xC$_2$Cl$_3$H + (1 − x)C$_4$H$_9$OH	−172.8837	64.7534	67.7933	1
xC$_2$Cl$_3$H + (1 − x)C$_5$H$_{11}$OH	−138.5624	21.9894	10.5519	1
xC$_2$Cl$_3$H + (1 − x)C$_6$H$_{13}$OH	−91.7152	47.3109	−6.2324	1
xC$_2$Cl$_3$H + (1 − x)C$_7$H$_{15}$OH	−76.0879	13.2188	36.8973	1
xC$_2$Cl$_3$H + (1 − x)C$_8$H$_{17}$OH	−56.3892	−0.1221	17.1922	1

The deviation in isentropic compressibilities, Δk_s, are negative over the whole range of composition for all the binary mixtures formed by trichloroethylene with the alkan-1-ols. The negative values of Δk_s for all the binary mixtures fall in the order

propan-1-ol ≈ butan-1-ol > pentan-1-ol > hexan-1-ol > heptan-1-ol > octan-1-ol

Acknowledgment

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