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Isentropic Compressibilities of Mixtures of Aliphatic Alcohols with Benzonitrile

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Isentropic compressibilities of binary mixtures of homologous series of aliphatic alcohols + benzonitrile were measured at 308.15 K and are reported here. The mixtures studied are 1-propanol + benzonitrile, 1-butanol + benzonitrile, 1-pentanol + benzonitrile, 2-propanol + benzonitrile, 2-methyl-1-propanol + benzonitrile, and 3-methyl-1-butanol + benzonitrile.

Introduction

These measurements were made as part of a study of isentropic compressibilities of a number of binary liquid mixtures (*1–5*). In this paper we report measurements of the isentropic compressibilities of a homologous series of aliphatic alcohols with a common solvent, benzonitrile, at 308.15 K. A literature survey showed that no one has reported isentropic compressibility data for these mixtures of six alcohols with benzonitrile at 308.15 K.

Experimental Section

Measurement of Density. Densities were measured by using a bicapillary pycnometer described by Rao (*6*) and were accurate to 5 parts in 10^5 parts. The pycnometer was similar to that of Parkar and Parkar with minor modifications. It was a double-stem pycnometer made of Pyrex glass and it consisted of a bulb that held about 11 cm^3. The stems were made of capillary tubing with a uniform bore of about 1 mm. The double-stem pycnometer was standardized by using triple-distilled water at 303.15 K.

Measurement of Ultrasonic Velocity. Ultrasonic velocities were measured by using a variable-path single-crystal interferometer. A crystal-controlled rf oscillator (high-frequency generator) was used to excite the transducer at a frequency of 2 MHz. The frequency was measured with an accuracy of 1 in 10^6 by using a digital frequency meter. The voltage variations across the transducer were observed by using a microammeter. Two controls were provided for the purpose of sensivity regulation and initial adjustment of the microammeter. The interferometer cell was filled with the experimental liquid and was connected to the output terminal of the high-frequency generator through a shielded cable. Water was circulated around the measuring cell from a thermostat maintained at 308.15 ± 0.01 K. When the liquid attained the temperature of the bath, the microammeter screw was slowly moved till the anode current meter showed a maximum.

For increasing the accuracy of the measurement, several such maxima were counted (n) by changing the distance between the transducer and the reflector. The total distance d moved by the reflector was used to calculate the wavelength, λ, by the equation $d = n\lambda/2$. The frequency of the crystal f being accurately known (1.995 MHz), the sound velocity, u, was calculated by the relation $u = \lambda f$. The sound velocities are accurate to 1 in 1000 m.

Determination of Isentropic Compressibility. The isentropic compressibilities were calculated from the relation

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

Table I. Boiling Points and Densities of Pure Components

component	bp, K present work	bp, K lit. (*7*)	ρ(303.15 K), g cm^{-3} present work	ρ(303.15 K), g cm^{-3} lit. (*7*)
1-propanol	370.15	370.15	0.795 60	0.795 67
1-butanol	390.15	390.22	0.802 05	0.802 06
1-pentanol	411.00	411.10	0.807 54	0.807 64
2-propanol	354.85	355.35	0.776 85	0.776 90
2-methyl-1-propanol	380.94	381.04	0.794 31	0.794 37
3-methyl-1-butanol	404.35	405.05	0.801 67	0.801 79
benzonitrile	463.93	464.04	0.996 19	0.996 28

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

Purification of Materials. Benzonitrile (Riedel) was dried over freshly fused calcium chloride for 2 days and distilled at atmospheric pressure.

1-Propanol (E. Merck) was refluxed over lime for 5 h and then distilled through a 1-m fractionating column. The fraction boiling at 370.15–370.35 K was collected.

1-Butanol (BDH) was refluxed over freshly ignited calcium oxide for 4 h. The alcohol was decanted from the lime, refluxed with magnesium turnings, and then fractionally distilled. The middle fraction which boiled at 390.75 K was collected.

1-Pentanol (E. Merck) was dried over Drierite and fractionally distilled.

2-Propanol (BDH) was dried first with calcium chloride and then with barium oxide and fractionally distilled.

2-Methyl-1-propanol (BDH) was purified by repeated fractional distillation through a 1-in.–90 plate column.

3-Methyl-1-butanol (BDH) was dried with calcium chloride and then purified by careful fractional distillation.

The purities of the chemicals were checked by comparing the values of densities at 303.15 K and boiling points corrected to 1-atm pressure with those reported in the literature (*7*) and are presented in Table I.

Results and Discussion

The values of isentropic compressibilities of mixtures and of pure components calculated from the measured values of sound velocities and densities were used to calculate the values of the parameter ΔK_s, by using the equation

$$\Delta K_s = K_s - \phi_A K_{s,A} - \phi_B K_{s,B} \qquad (2)$$

where K_s, $K_{s,A}$, and $K_{s,B}$ are the isentropic compressibilities of the mixture and the pure components A and B, and ϕ_A and ϕ_B are the volume fractions of components A and B, respectively. The values of ΔK_s for the six systems are presented in Table II and represented in Figures 1 and 2.

Values of ΔK_s for the six systems are negative over the entire range of compositions in all of the systems. The negative values of ΔK_s in the mixtures of benzonitrile with primary straight-chain alcohols fall in the following order:

1-propanol > 1-butanol > 1-pentanol

The negative values of ΔK_s in the mixtures of benzonitrile with the remaining alcohols also fall in the same order:

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

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Table II. Isentropic Compressibilities of Aliphatic Alcohols with Benzonitrile at 308.15 K

ϕ_A[a]	ρ,[b] g cm^{-3}	u,[c] m s^{-1}	K_s,[d] TPa^{-1}	ΔK_s,[e] TPa^{-1}	δK_s,[f] TPa^{-1}
Benzonitrile + 1-Propanol					
0.0000	0.791 90	1171	921		
0.1134	0.821 00	1207	837	−33	+1
0.3007	0.855 31	1245	754	−49	−3
0.4391	0.882 94	1274	698	−52	+1
0.5780	0.910 48	1301	649	−46	+1
0.7075	0.935 56	1326	608	−37	+2
0.8194	0.957 65	1346	577	−24	−1
0.9262	0.977 91	1367	547	−12	0
1.0000	0.991 98	1378	531		
Benzonitrile + 1-Butanol					
0.0000	0.798 10	1203	866		
0.1090	0.820 98	1229	806	−24	−1
0.2496	0.848 98	1257	746	−37	0
0.3886	0.877 73	1279	696	−40	0
0.5241	0.901 74	1304	652	−38	0
0.6653	0.928 04	1328	611	−32	+3
0.7906	0.952 57	1346	579	−22	+1
0.9099	0.975 01	1365	550	−11	0
1.0000	0.981 98	1378	531		
Benzonitrile + 1-Pentanol					
0.0000	0.803 69	1238	812		
0.1331	0.829 46	1264	756	−18	0
0.1778	0.837 99	1269	741	−21	0
0.2761	0.856 71	1283	709	−26	−1
0.3792	0.876 29	1298	677	−29	+1
0.4261	0.885 08	1304	664	−29	+1
0.4435	0.888 29	1306	650	−28	0
0.5270	0.904 11	1317	637	−27	0
0.5754	0.913 11	1323	625	−25	0
0.6287	0.922 99	1329	613	−22	−1
0.7284	0.941 53	1345	587	−20	+1
0.8671	0.967 25	1361	558	−10	0
1.0000	0.991 98	1378	531		
Benzonitrile + 2-Propanol					
0.0000	0.772 76	1102	1066		
0.1303	0.802 50	1149	942	−54	0
0.2284	0.824 75	1183	867	−76	+1
0.2950	0.839 51	1200	827	−81	−1
0.4238	0.867 79	1237	754	−84	+1
0.5080	0.886 05	1259	712	−80	+1
0.6210	0.899 57	1287	671	−68	0
0.7143	0.930 16	1311	625	−55	0
0.7943	0.948 42	1331	595	−43	0
0.8735	0.964 29	1349	570	−28	+1
1.0000	0.991 98	1378	531		
Benzonitrile + 2-Methyl-1-propanol					
0.0000	0.790 25	1154	950		
0.1316	0.817 68	1191	863	−32	0
0.2300	0.837 81	1216	807	−47	0
0.3466	0.861 57	1244	749	−56	+1
0.4016	0.872 63	1256	726	−55	−1
0.5056	0.893 45	1279	684	−54	0
0.6293	0.918 09	1304	640	−46	−1
0.6959	0.931 31	1321	615	−43	+1
0.8049	0.953 05	1342	582	−30	0
0.8666	0.965 26	1353	566	−21	0
1.0000	0.991 98	1378	531		
Benzonitrile + 3-Methyl-1-butanol					
0.0000	0.798 20	1203	867		
0.1269	0.822 76	1229	805	−20	0
0.2285	0.843 16	1250	758	−31	+1
0.3332	0.863 58	1269	719	−36	+1
0.4320	0.882 64	1286	685	−37	0
0.5252	0.900 64	1303	654	−37	+1
0.5682	0.908 94	1310	641	−35	+1
0.5954	0.913 66	1314	634	−33	0
0.7161	0.937 29	1334	599	−27	0
0.8030	0.954 00	1345	580	−20	0
0.8689	0.966 62	1359	560	−15	+1
1.0000	0.991 98	1378	531		

[a] Volume fraction of benzonitrile. [b] Density. [c] Sound velocity. [d] Values of K_s calculated from u and ρ. [e] Values of ΔK_s computed from eq 2. [f] $\delta K_s = \Delta K_{s,\mathrm{exptl}} - \Delta K_{s,\mathrm{calcd(eq\ 3)}}$.

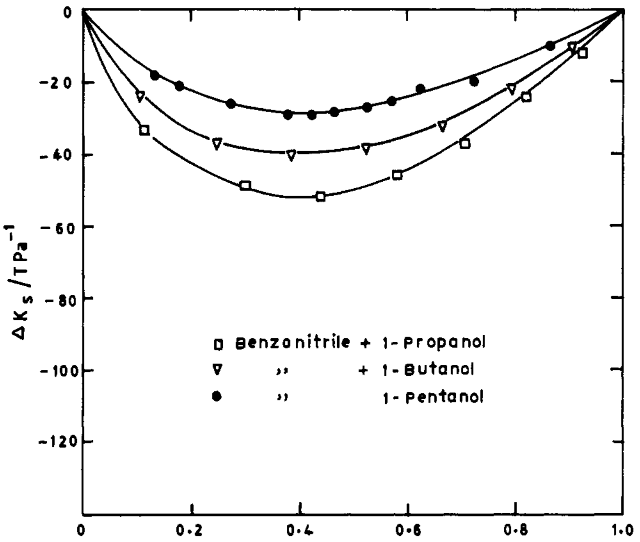

Figure 1. Parameter ΔK_s–volume fraction curves for (□) 1-propanol, (▽) 1-butanol, and (●) 1-pentanol with benzonitrile at 308.15 K.

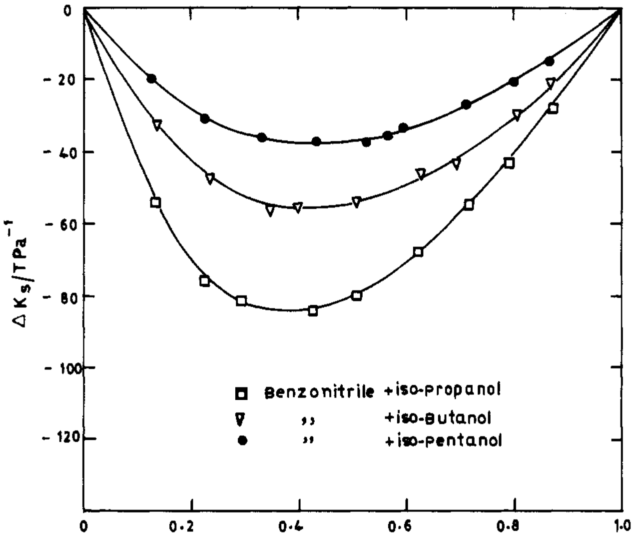

Figure 2. Parameter ΔK_s–volume fraction curves for (□) 2-propanol, (▽) 2-methyl-1-propanol, and (●) 3-methyl-1-butanol with benzonitrile at 308.15 K.

The dependence of ΔK_s on composition may be represented in terms of a power series

$$\Delta K_s/(\phi_A\phi_B) = b_0 + b(\phi_A - \phi_B) + b_2(\phi_A - \phi_B)^2 \qquad (3)$$

where ϕ_A and ϕ_B are volume fractions of components A and B, and b_0, b_1, and b_2 are arbitrary constants whose values have been obtained by the least-squares principle. Values of

Table III. Standard Deviation (σ) and Values of the Constants in Eq 3 at 308.15 K[a]

system	b_0	b_1	b_2	σ
benzonitrile + 1-propanol	−196.01	96.40	−85.39	2
benzonitrile + 1-butanol	−148.71	68.60	−57.21	1
benzonitrile + 1-pentanol	−108.90	43.38	−21.40	1
benzonitrile + 2-propanol	−320.48	150.55	−84.44	1
benzonitrile + 2-methyl-1-propanol	−218.90	66.60	−26.83	1
benzonitrile + 3-methyl-1-butanol	−144.03	37.25	−15.47	1

[a] All values in TPa^{-1}.

these constants are given in Table III along with the standard deviation, σ, which is obtained by using the equation

$$\sigma = \left[\frac{\sum(\Delta K_{s,\mathrm{exptl}} - \Delta K_{s,\mathrm{calcd}})^2}{n-p}\right]^{1/2} \tag{4}$$

where n is the number of results and p is the number of parameters in eq 3.

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Speed of Sound in Saturated Liquid *n*-Pentane

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The speed of sound in saturated liquid *n*-pentane has been measured in the temperature range −70 to 35 °C from 7.3 to 12 MHz. Two different methods were used, and the agreement of the two data sets is within the experimental error. These data were combined with available density data to obtain the adiabatic compressibilities.

Introduction

Measurements of the speed of sound offer a convenient method for determining certain thermodynamic properties of dense fluids not easily obtained by other means. We have measured the speed of sound W in saturated liquid n-pentane from −70 to 35 °C using the pulse-echo-superposition (PES) and pulse-echo-overlap (PEO) methods at frequencies from 7.3 to 12 MHz. The results have been used with the available density ρ_σ data to obtain isentropic compressibility β_S by means of the relation $W^2 = (\rho_\sigma\beta_s)^{-1}$.

Experimental Procedure

The speed of sound was measured by using two different methods. The first was the pulse-echo superposition (PES), used previously in this laboratory for measurements on trichlorofluoromethane (*1*) and described previously (*1*, *2*). The second method, used widely in solids (*3*, *4*), was the pulse-echo overlap (PEO) described in detail elsewhere (*3*, *5*). Measurements were made by using two 10-MHz X-cut quartz crystals. The first data set was obtained by using the PES method where the crystals vibrated at their resonant frequencies. In the second data set, obtained with the PEO method, at each temperature, the crystals were forced to vibrate around two frequencies, 7.3 and 12 MHz, at which the observed signal on the oscilloscope was clearer. The differences in the overlapping criteria with these frequencies were always less than 10 Hz in the repetition rate frequency. This corresponds to less than 0.02% in the measured speed of sound. This, together with the uncertainties in the acoustic path length and pulse repetition frequency, gives an uncertainty in the measured speed of sound of less than 0.05%, which is comparable with that estimated for the PES method.

The sample cell made of heavy copper was immersed in a thermostated ethanol bath which was controlled with a sensitive proportional temperature regulation. Temperatures were measured by using platinum resistance thermometer calibrated on the IPTS-68. This thermometer was located in a thermowell inside the sample cell in contact with the liquid n-pentane. The temperature could be maintained within ±0.006 °C during the measurements. The n-pentane used was commercially obtained from Merck with reported minimum purity of 99.0% and probable impurities of water and sulfur compounds. The n-pentane was not further purified except for the degassing performed at 25 °C. At each temperature, the sound speed was measured at least twice with some n-pentane being removed from the sample cell between the measurements. Identical sound speed observations indicated that the two-phase condition existed in the sample cell.

Results and Discussion

The speed of sound for the saturated liquid n-pentane has been measured at about 5 °C intervals from −70 to 35 °C for both data sets. These data are shown in Table I. For the PEO method the data are those obtained with the crystals vibrating around 12 MHz. The speed of sound data set measured with the PES method was fitted to a quadratic equation of the form

$$W(t) = a + bt + ct^2 \tag{1}$$

where, a b, and c were found by an unweighted least-squares method. The coefficients obtained are a = 1126.257, b = −4.935006, and c = 0.0016748. Deviations of the two data

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