

Registry No. 1-Propanol, 71-23-8; 1-butanol, 71-36-3; 1-hexanol, 111-27-3; 1-octanol, 111-87-5; 1-decanol, 112-30-1; hexene, 110-54-3.

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Speed of Sound in and Isothermal Compressibility and Isobaric Expansivity of Pure Liquids at 298.15 K

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The speed of sound u , the isothermal compressibility κ_T , and the isobaric expansivity α have been determined at 298.15 K for several hydrocarbons containing 5, 6, 10, and 12 carbon atoms. Values of the isentropic compressibility κ_S were also calculated from the speed of sound experimental results.

Introduction

The isothermal compressibility $\kappa_T = -V^{-1}(\partial V/\partial p)_T$ and the isobaric expansivity $\alpha = V^{-1}(\partial V/\partial T)_p$ together with the molar volume V are thermodynamic properties used in recent theories of liquids to calculate the characteristic parameters P^* , V^* , and T^* of pure substances. Currently, Letcher and Baxter (1) are studying the Flory theory of mixtures including the substances we measure in this paper, so experimental data of κ_T and α are indispensable. In this work we report results of κ_T , α , and u for several substances containing six carbon atoms and for others including aromatic and nonaromatic rings.

Experimental Section

The solvents 1-hexene and 1-hexyne from Fluka and cyclohexene, cyclopentane, and cyclohexylbenzene from Aldrich

were distilled and dried. Bicyclohexyl (EGA Chemic), 1,3-cyclohexadiene (Aldrich), 1,4-cyclohexadiene (Aldrich), and tetralin (BDH) were used without further purification. Their purities, determined by gas liquid chromatography, were 98% for cyclohexylbenzene and 1,4-cyclohexadiene and better than 99% for the other. Experimental densities at 298.15 K were determined with a Paar densimeter and are reported in Table I.

The experimental methods used in measuring κ_T and α (direct piezometric technique), including the piezometer filling, and in measuring u (pulse-echo-overlap method) have been described elsewhere (2-6). Values of κ_T and α are obtained with a precision better than 0.2% while the precision of u is better than 0.1 m·s⁻¹.

Results and Discussion

Measurements of isothermal compressibility κ_T , and isobaric expansivity α at 298.15 K were run twice. Table I reports average values of those thermodynamic magnitudes for several hydrocarbons containing 5, 6, 10, and 12 carbon atoms. The speed of sound u has been determined by action of waves of 2.25 MHz on the same substances, and the results obtained are also reported in Table I. In that table are values for the same

Table I. Experimental Results of Pure Liquids at 298.15 K

substance	ρ^a	κ_T^b	$10^3\alpha^c$	u^d	κ_S^e
n-hexane	655.04	1669 ^f	1.381 ^j	1076.78 ^l	1316.68
1-hexene	669.01	1689 (1711) ^g	1.414	1066.06 (1065) ^m	1315.24
1-hexyne	729.29	1404	1.371	1132.35 (1140) ^m	1069.40
cyclopentane	737.36	1332 (1331) ^h	1.351 (1.347) ^h	1200.89	940.40
cyclohexane	773.87	1120 ⁱ	1.215 ^h	1253.86 ^l	821.93
cyclohexene	805.88	1036 (1041) ^g	1.177	1274.44 (1278) ^m	764.00
1,3-cyclohexadiene	841.60	962 (1012) ^g	1.142	1279.03	726.33
1,4-cyclohexadiene	851.03	944 (917) ^g	1.141	1326.40	667.89
benzene	873.69	966 ^f	1.218 ^j	1299.40 ^l	677.78
bicyclohexyl	882.73	674	0.819 (0.784) ^k	1441.51	545.17
cyclohexylbenzene	938.97	627	0.818 (0.753) ^k	1458.11 (1457) ^m	500.92
tetralin	964.55	607	0.824 (0.745) ^k	1469.29 (1466) ^m	480.24

^aIn kg·m⁻³. ^bIn TP·a⁻¹. ^cIn K⁻¹. ^dIn m·s⁻¹. ^eIn TP·a⁻¹. ^fReference 4. ^gReference 8. ^hReference 7. ⁱReference 9. ^jReference 10. ^kReference 1. ^lReference 6. ^mReference 11. The other values have been measured in this work.

three thermodynamic properties for *n*-hexane, cyclohexane, and benzene measured previously by us (4, 6, 9, 10). Results of this work are compared with the literature data (in parentheses). All results are in agreement with literature data except α for bicyclohexyl, cyclohexylbenzene, and tetralin. This is due to the fact that our values of α at 298.15 K are obtained by measuring 12 volumes between 296.65 and 299.65 K while Letcher and Baxter (1) obtain them with less measurements of density and in a wider range of temperatures (between 283.15 and 313.15 K).

The isentropic compressibility $\kappa_S = -V^{-1}(\partial V/\partial p)_S$ is related to the speed of sound through the density ρ of the substance by

$$\kappa_S = 1/\rho u^2 \quad (1)$$

Values of κ_S calculated for all substances measured in this work are reported in the last column of Table I. Results of the internal pressure coefficient $\gamma = \alpha/\kappa_T$ can be easily obtained from the data of Table I, and the values are therefore omitted.

Registry No. Hexane, 110-54-3; 1-hexene, 592-41-6; 1-hexyne, 693-02-7; cyclopentane, 287-92-3; cyclohexane, 110-82-7; cyclohexene,

110-83-8; 1,3-cyclohexadiene, 592-57-4; 1,4-cyclohexadiene, 628-41-1; benzene, 71-43-2; bicyclohexyl, 92-51-3; cyclohexylbenzene, 827-52-1; tetralin, 119-84-2.

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Excess Volumes, Ultrasonic Sound Velocities, and Isentropic Compressibilities of 1-Chlorobutane with Isopropyl, Isobutyl, and Isopentyl Alcohols

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New experimental data on excess volumes, sound velocities, and isentropic compressibilities for the mixtures of 1-chlorobutane with isopropyl, isobutyl, and isopentyl alcohols are reported. The sound velocities have been analyzed in terms of free length theory (FLT) and collision factor theory (CFT). The positive excess volumes and positive deviations in isentropic compressibilities have been attributed to the dissociation of self-associated alcohols and chlorobutane.

Introduction

Excess volumes, sound velocities, and isentropic compressibilities of 1-chlorobutane with normal alcohols have been reported by us (1, 2). To study the effect of branching of alcohols on these properties, further measurements on excess volumes, sound velocities, and isentropic compressibilities have been carried out. We report here excess volumes (at 303.15 and 313.15 K), sound velocities, and isentropic compressibilities (at 303.15 K) of 1-chlorobutane with isoalcohols. The isoalcohols include isopropyl, isobutyl, and isopentyl alcohols. The sound velocities have been analyzed in terms of Jacobson's free length theory (FLT) (3, 4) and Schaaf's collision factor theory (CFT) (5, 6).

Table I. Boiling Points and Densities of Pure Components along with the Literature Values

component	boiling point/K		density(303.15 K)/(g·cm ⁻³)	
	expt	lit. (10)	expt	lit. (11)
1-chlorobutane	381.40	381.59	0.87543	0.87549
isopropyl alcohol	385.20	385.41	0.77692	0.77690
isobutyl alcohol	410.55	410.81	0.79439	0.79437
isopentyl alcohol	433.30	433.65	0.80177	0.80179

Experimental Section

Excess volume (V_m^E) was measured by using the batch dilatometers described earlier (7, 8). The mixing cell contained two bulbs of different capacities that were connected through a U-tube having mercury to separate the two compartments. One end of the first bulb was fitted with a capillary outlet and the opposite end of the second bulb was closed with a ground glass stopper. Four dilatometers of this type were used to cover the whole range of composition. The composition of each mixture was determined directly by weighing. All weights were corrected for buoyancy. The V_m^E values were accurate to ± 0.003 cm³·mol⁻¹. The ultrasonic sound velocity was measured with a single-crystal interferometer at a frequency