

Speeds of sound and isothermal compressibility of ternary liquid systems: Application of Flory's statistical theory and hard sphere models

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Abstract. Speeds of sound and densities of three ternary liquid systems namely, toluene + *n*-heptane + *n*-hexane (I), cyclohexane + *n*-heptane + *n*-hexane (II) and *n*-hexane + *n*-heptane + *n*-decane (III) have been measured as a function of the composition at 298.15 K at atmospheric pressure. The experimental isothermal compressibility has been evaluated from measured values of speeds of sound and density. The isothermal compressibility of these mixtures has also been computed theoretically using different models for hard sphere equations of state and Flory's statistical theory. Computed values of isothermal compressibility have been compared with experimental findings. A satisfactory agreement has been observed. The superiority of Flory's statistical theory has been established quite reasonably over hard sphere models.

Keywords. Flory's statistical theory; hard sphere models; isothermal compressibility; ternary liquid systems.

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1. Introduction

The primary objective is to measure the speeds of sound and density of liquid systems in order to estimate the value of isentropic compressibility (β_S). This cannot be done by any other method. Isentropic compressibility has been widely used to study the molecular interactions through its excess value. On the other hand, it can also be used to deduce other useful thermodynamic properties such as isothermal compressibility (β_T), heat capacity ratio (γ), internal pressure (p_i) and cohesive energy density (CED). Isothermal compressibility and heat capacity ratios are two key parameters in molecular thermodynamics of fluid phase equilibria. Various hard sphere equations of state and Flory's statistical theory have been applied to evaluate the values of isothermal compressibility, specific heat ratio (β_T , γ) and speeds of sound (u) of pure liquids under varying physical conditions [1,2].

Such theories were also applied to binary liquid mixtures for estimating isothermal compressibility and speeds of sound by a few workers [3]. The theoretical values of β_T have also been compared with the experimental values, obtained from β_S , α and C_P data. Direct measurement of β_T for a few binary mixtures had also been reported in [4–6].

In the present work, the results of experimental measurement of speeds of sound (u) and density (ρ) of three ternary liquid systems namely, toluene + n -heptane + n -hexane (I); cyclohexane + n -heptane + n -hexane (II) and n -hexane + n -heptane + n -decane (III) have been reported at 298.15 K. Further, density and speeds of sound data were used to evaluate experimental isothermal compressibility (β_T) with the help of empirical equation derived. Theoretical isothermal compressibility (β_T) values were estimated with the help of various important hard sphere models. Another approach, i.e. Flory's statistical theory [7,8] was also used for computing theoretical β_T values of three ternary liquid systems under the present investigation. The theoretical β_T values are compared with the experimental β_T values deduced from the derived empirical equation. This is a novel theoretical approach for estimating the isothermal compressibility of ternary liquid systems containing n -alkanes, which are best suited for practical engineering use. The isothermal compressibility data of these industrially important organic compounds of ternary and higher liquid systems are very scarce, because of the difficulty arising in their calculations.

2. Experimental procedure

All the organic liquids used were of analytical reagent grade and were obtained from BDH Chemicals Ltd, England. These chemicals were further purified by double distillation. Densities and speeds of sound were measured at 298.15 K. Densities were determined with a precalibrated bicapillary pycnometer with an accuracy of $\pm 0.3 \text{ kg/m}^3$ ($\sim 0.05\%$). Speeds of sound measurement were made with a single crystal variable path ultrasonic interferometer (Model F-81; 'Mittal' make) at 2 MHz frequency with an accuracy of $\pm 0.01\%$.

The purity of the samples and accuracy of data were checked by comparing the measured density of the compounds with those reported in [9].

3. Theoretical considerations

In the present investigation, the following expressions representing five hard sphere models [10–16], used for the computation of theoretical isothermal compressibility of ternary liquid systems:

(1) *Thiele Lebowitz model:*

$$\beta_T = \frac{V}{RT} \frac{(1-y)^4}{(1+2y)^2}. \quad (1)$$

(2) *Thiele model:*

$$\beta_T = \frac{V}{RT} \frac{(1-y)^3}{(1+5y+9y^2-3y^3)}. \quad (2)$$

(3) *Carnahan-Starling model:*

$$\beta_T = \frac{V}{RT} \frac{(1-y)^4}{(1+4y+4y^2-4y^3+y^4)}. \quad (3)$$

(4) *Guggenheim model:*

$$\beta_T = \frac{V}{RT} \frac{(1-y)^5}{(1+3y)}. \quad (4)$$

(5) *Hoover-Ree model:*

$$\beta_T = \frac{V}{RT} (1+8y+30y^2+73.44y^3+141.0y^4+273.04y^5)^{-1}, \quad (5)$$

where V , R , T , and y are the molar volume, the gas constant, absolute temperature and packing fraction respectively.

The packing fraction y is defined as

$$y = \frac{\pi d^3 N}{6V}, \quad (6)$$

where d is the rigid sphere diameter of the molecules comprising the pure liquid and liquid mixture and all other symbols have their usual meanings. The value of d is obtained by using the values of speeds of sound, in a manner similar to that described elsewhere [17].

Flory's statistical theory gives the following expression [7,8] for the evaluation of theoretical isothermal compressibility of ternary liquid systems:

$$\beta_T = \frac{\alpha T \tilde{v}^2}{p^*}, \quad (7)$$

where α is the coefficient of thermal expansion, T is the temperature in Kelvin, \tilde{v} and p^* are respectively the reduced volume and characteristic pressure of the liquid mixture. Values of \tilde{v} and p^* were evaluated by the procedure detailed out by Flory and used by us in our earlier papers [18-20].

In 1966, Mc-Gowan [21] suggested the following relationship between isothermal compressibility and surface tension (σ):

$$\beta_T \sigma^{3/2} = 1.33 \times 10^{-8} \text{ (cgs units)}. \quad (8)$$

The Auerbach relationship [22] between speed of sound (u) and surface tension (σ) is as follows:

$$u = \left[\frac{\sigma}{6.3 \times 10^{-4} \rho} \right]^{2/3}. \quad (9)$$

Table 1. Density (ρ) and speeds for sound (u) for the component liquids at 298.15 K.

Component liquids	$\rho \times 10^{-3}$ (g m ⁻³)		u (m s ⁻¹)	
	Present study	Literature	Present study	Literature
Toluene	0.8626	0.8625	1304.3	1304.3
Cyclohexane	0.7736	0.7738	1252.0	1253.3
<i>n</i> -Hexane	0.6548	0.6550	1075.8	1076.0
<i>n</i> -Heptane	0.6790	0.6795	1131.0	1131.0
<i>n</i> -Decane	0.7260	0.7263	1225.0	1225.2

Table 2. Thermal expansion coefficient (α), isothermal compressibility (β_T), reduced molar volume (\tilde{v}), characteristic molar volume (v^*) and characteristic pressure (p^*) for the component liquids at 298.15 K.

Component liquids	$\alpha \times 10^{-3}$ (K ⁻¹)	$\beta_T \times 10^{12}$ (N ⁻¹ m ²)	$\tilde{v} \times 10^6$ (cm ³ mol ⁻¹)	$v^* \times 10^6$ (cm ³ mol ⁻¹)	$\rho^* \times 10^9$ (N m ⁻²)
Toluene	1.0740	681.70	1.2627	84.5867	0.5540
Cyclohexane	1.2150	824.90	1.2902	84.2920	0.5290
<i>n</i> -Hexane	1.3897	1313.3	1.3224	99.4706	0.4511
<i>n</i> -Heptane	1.2589	1151.2	1.2985	113.6375	0.4444
<i>n</i> -Decane	1.0500	917.90	1.2579	155.7700	0.4259

These two equations have been employed by a number of workers during recent years [18–20] in the case of pure liquids, solutions of non-electrolytes, molten salts and liquid metals.

By combining the above two equations, we get the following expression for the evaluation of experimental isothermal compressibility:

$$\beta_T = \frac{1.33 \times 10^{-8}}{(6.3 \times 10^{-4} u^{3/2} \rho)^{3/2}} \quad (10)$$

This expression gives a direct relationship between isothermal compressibility, speed of sound and density and has been tested for a variety of pure liquids and binary liquid systems under varying physical conditions.

4. Results and discussion

The measured densities and speeds of sound for pure component liquids along with the literature values are presented in table 1. The agreement between the two sets of values is very good. The values of the important thermodynamic parameters of pure component liquids have been recorded in table 2. Density and speeds of sound of three ternary liquid systems (I–III) have been measured as a function of composition at 298.15 K and the values are recorded in columns three and four of tables 3–5.

Speeds of sound and density data, obtained for all the three ternaries, have been utilized to estimate the values of experimental isothermal compressibility (β_T), with the help of empirical equation derived (eq. (10)). These values are reported in column five of each table (tables 3–5), for the respective systems mentioned.

The required experimental data, for the computation of theoretical isothermal compressibility of three ternary liquid systems from Flory's statistical theory and hard sphere models, have been generated in our laboratory [23]. Theoretical isothermal compressibility (β_T) of all three ternary liquid systems have been computed with the help of Flory's statistical theory and five hard sphere models at 298.15 K.

Two sets of data are generated from computation of theoretical isothermal compressibility β_T for all the ternary systems. In one set, the values of isothermal compressibility have been computed on the basis of various hard sphere equations of state by using eqs (1)–(5) and presented in columns (6)–(10) of each table (tables 3–5). A second set of theoretical β_T values, which are computed from Flory's statistical theory using eq. (7) are recorded in the last column of each table (tables 3–5).

In the case of system (I), toluene + *n*-heptane + *n*-hexane, the experimental values of β_T decrease continuously on increasing the mole fraction of the first component (toluene). A similar trend is also observed theoretically, as is evident from the result of columns 6–10 of table 3. The values of β_T computed from Flory's theory for this system also show a similar trend (last column of table 3).

In the case of system (II), cyclohexane + *n*-heptane + *n*-hexane, the experimental and theoretical values of β_T show similar trend. The values of β_T decrease continuously on increasing the mole fraction of the first component ((cyclohexane), table 4).

A close perusal of table 4 shows that the system (III), *n*-hexane + *n*-heptane + *n*-decane does not show exactly similar trend of variation in β_T values as in the case of systems (I) and (II). No regular increase or decrease is observed. All the theoretical and experimental values, including values computed from Flory's theory show similar behavior. The probable reason for this is that, in this system *n*-decane is present as a third component.

Table 6 lists the average percentage deviations obtained in theoretical isothermal compressibility values for all the systems under investigation. From this table, it was observed that Flory's statistical theory provides good agreement with the experimental values for the system (I) toluene + *n*-heptane + *n*-hexane, deviations being not more than 0.66%. A similar trend has been followed by Thiele's model (eq. (2)), the observed deviations being not more than –9.30%. This trend is further followed by the Carnahan–Starling model (eq. (3)) and the Hoover–Ree model (eq. (5)), both the models give satisfactory agreement with the experimental values, the observed deviations being not more than 11.77% and –11.23%. The Guggenheim model (eq. (4)) gives maximum deviation with experimental values.

In the case of system (II) cyclohexane + *n*-heptane + *n*-hexane, Flory's statistical theory gives better agreement with the experimental values, deviations being not more than 0.88%. A similar trend has been provided by Thiele's model (eq. (2)) and Hoover–Ree model (eq. (5)) also, deviations being not more than –3.77% and –4.43% respectively.

Table 3. Density, speeds of sound and isothermal compressibility of ternary system (I): toluene (x_1) + n -heptane (x_2) + n -hexane (x_3) at 298.15 K. $x_3 = 1 - (x_1 + x_2)$.

Mole fraction		$\beta_T \times 10^{12}$ (Theoretical) ($\text{m}^2 \text{N}^{-1}$)								
x_1	x_2	$\rho \times 10^{-3}$ (g m^{-3})	u (m s^{-1})	$\beta_T \times 10^{12}$ ($\text{m}^2 \text{N}^{-1}$) (Exptl)	$\beta_T \times 10^{12}$ (Theoretical)					Flory's
					Eq. (1) (TL)	Eq. (2) (T)	Eq. (3) (CS)	Eq. (4) (G)	Eq. (5) (HR)	Eq. (7)
0.1210	0.1838	0.7506	1106.2	183.27	138.66	186.02	151.52	118.58	187.77	184.10
0.1459	0.2011	0.7529	1112.1	180.26	137.06	184.26	149.26	117.05	186.27	181.61
0.1698	0.2170	0.7570	1116.9	177.08	136.48	183.57	149.24	116.52	185.63	178.47
0.1929	0.2358	0.7635	1120.0	173.04	134.60	181.33	147.25	114.25	184.80	174.32
0.2160	0.2544	0.7682	1128.3	169.31	133.00	179.48	145.57	113.32	181.91	170.94
0.2390	0.2726	0.7733	1133.8	165.81	131.44	177.65	143.39	111.88	180.25	166.73
0.2641	0.2875	0.7791	1139.9	163.04	126.26	174.85	142.45	109.65	178.65	166.28
0.2849	0.3000	0.7835	1145.3	158.93	128.27	173.92	140.57	108.96	176.87	159.56
0.3088	0.3222	0.7849	1151.5	156.59	127.49	173.11	138.77	108.20	176.21	157.58
0.3330	0.3391	0.7938	1158.0	152.03	125.00	170.06	137.09	105.94	173.38	153.49
0.3559	0.3553	0.8000	1164.4	148.41	123.10	167.82	135.10	104.22	171.33	149.87
0.3760	0.3735	0.8036	1170.3	145.75	121.90	166.69	133.28	103.21	169.32	146.29
0.3983	0.3908	0.8089	1177.2	142.42	120.15	164.38	131.98	101.49	168.26	143.30
0.4204	0.3974	0.8188	1183.0	138.31	117.42	161.00	129.07	99.05	165.08	139.32
0.4439	0.4045	0.8324	1189.6	133.26	114.28	157.04	125.69	96.26	161.28	134.45

In the case of system (III), n -hexane + n -heptane + n -decane, Flory's statistical theory provides good agreement, deviations being not more than 7.99%. Thiele's model (eq. (2)), Carnahan–Starling model (eq. (3)) and Hoover–Ree model (eq. (5)) also give reasonable agreement with the experimental values.

5. Conclusions

In summary, we conclude that:

1. The present investigation successfully demonstrated the superiority of Flory's statistical theory over hard sphere models in all the ternary liquid systems. Thiele's model also provides good agreement with Flory's statistical theory and experimental values of isothermal compressibility. This observation is followed by Carnahan–Starling and Hoover–Ree models. In these hard sphere models, attractive and repulsive forces are taken into account and it is useful for exploratory calculations.
2. The experimental isothermal compressibility values are quite comparable with the theoretical values obtained from Flory's statistical theory and hard sphere models. A reasonable agreement has been observed
3. We can use speeds of sound measurements not only for detecting molecular interactions, but also to obtain experimental isothermal compressibility values, which are very difficult to measure directly beyond binaries.

Table 4. Density, speeds of sound and isothermal compressibility of ternary system (II): cyclohexane (x_1) + n -heptane (x_2) + n -hexane (x_3) at 298.15 K. $x_3 = 1 - (x_1 + x_2)$.

Mole fraction		$\beta_T \times 10^{12}$ (Theoretical) ($\text{m}^2 \text{N}^{-1}$)								
x_1	x_2	$\rho \times 10^{-3}$ (g m^{-3})	u (m s^{-1})	$\beta_T \times 10^{12}$ ($\text{m}^2 \text{N}^{-1}$) (Exptl)	Eq. (1) (TL)	Eq. (2) (T)	Eq. (3) (CS)	Eq. (4) (G)	Eq. (5) (HR)	Flory's theory Eq. (7)
0.1189	0.1823	0.6832	1101.8	212.95	157.27	209.51	171.53	135.07	208.78	206.17
0.1440	0.2012	0.6863	1107.1	209.24	155.64	207.62	169.81	133.62	207.79	198.09
0.1650	0.2202	0.6897	111.3	205.93	154.15	205.88	168.24	132.19	206.08	196.80
0.1879	0.2379	0.6922	1115.0	203.29	153.10	204.65	167.17	131.21	204.82	192.94
0.2062	0.2484	0.6943	1119.0	200.75	151.92	203.27	165.89	130.12	201.86	192.72
0.2346	0.2729	0.6979	1126.1	196.38	147.99	200.03	161.77	127.44	200.92	192.06
0.2564	0.2903	0.6999	1129.5	194.22	149.10	198.80	162.93	126.54	199.96	189.88
0.2799	0.3073	0.7036	1135.1	190.56	147.28	197.89	161.01	125.83	199.96	188.50
0.3031	0.3266	0.7072	1140.2	187.21	145.67	196.00	159.31	124.35	198.24	187.02
0.3249	0.3424	0.7098	1144.7	184.53	144.43	194.55	158.00	123.20	196.92	185.42
0.3487	0.3599	0.7129	1150.6	181.22	142.80	192.64	154.83	121.69	195.20	183.07
0.3700	0.3776	0.7157	1155.5	177.45	141.47	191.09	154.33	120.46	193.80	182.19
0.3933	0.3948	0.7190	1161.9	175.03	139.68	188.99	152.98	118.81	191.90	180.63
0.4143	0.4030	0.7217	1164.8	173.07	137.52	187.52	151.70	116.38	189.96	179.30
0.4364	0.4103	0.7240	1169.2	170.80	133.56	186.42	150.72	115.89	188.51	177.77

Table 5. Density, speeds of sound and isothermal compressibility of ternary system (III): n -hexane (x_1) + n -heptane (x_2) + n -decane (x_3) at 298.15 K. $x_3 = 1 - (x_1 + x_2)$.

Mole fraction		$\beta_T \times 10^{12}$ (Theoretical) ($\text{m}^2 \text{N}^{-1}$)								
x_1	x_2	$\rho \times 10^{-3}$ (g m^{-3})	u (m s^{-1})	$\beta_T \times 10^{12}$ ($\text{m}^2 \text{N}^{-1}$) (Exptl)	Eq. (1) (TL)	Eq. (2) (T)	Eq. (3) (CS)	Eq. (4) (G)	Eq. (5) (HR)	Flory's theory Eq. (7)
0.1735	0.2759	0.7167	1125.4	188.97	170.31	233.94	187.83	143.50	240.18	191.43
0.2199	0.3692	0.7130	1115.0	194.46	171.06	232.82	187.66	144.97	237.41	188.78
0.2260	0.3185	0.7128	1110.3	196.40	170.17	232.45	186.85	143.90	237.62	190.59
0.2759	0.3158	0.7105	1105.6	199.25	170.02	232.61	187.58	145.00	237.15	190.80
0.3213	0.3524	0.7074	1101.4	202.29	165.80	229.91	181.50	141.20	227.05	184.64
0.3378	0.4849	0.7071	1100.1	202.95	170.09	230.32	186.24	144.62	233.99	189.86
0.3464	0.5192	0.7050	1099.8	203.99	164.70	228.93	179.55	140.12	223.48	185.19
0.3563	0.2797	0.7047	1098.6	204.62	170.79	231.50	187.15	145.11	235.36	192.83
0.3569	0.4377	0.7046	1096.2	205.67	165.45	223.25	181.90	140.97	226.26	187.55
0.3676	0.3504	0.7029	1095.8	206.59	169.24	228.62	185.07	144.10	231.88	190.35
0.3854	0.5504	0.7022	1093.4	207.92	162.50	218.26	177.82	139.19	223.48	184.44
0.4019	0.4291	0.7007	1093.0	208.76	166.36	223.71	181.08	142.05	226.18	187.76
0.4069	0.3878	0.6980	1092.4	210.23	166.78	224.59	182.43	142.28	227.30	189.76
0.4258	0.5421	0.6964	1092.0	211.13	161.50	216.28	176.38	138.26	220.28	183.56
0.4500	0.5179	0.6947	1090.3	212.65	162.59	216.85	177.99	139.31	219.01	180.99
0.4737	0.4943	0.6937	1088.9	213.73	162.14	215.22	176.99	138.91	218.41	185.56

Table 6. Average percentage deviation of theoretical isothermal compressibility with experimental β_T values at 298.15 K.

Ternary liquid systems	Eq. (1) (TL)	Eq. (2) (T)	Eq. (3) (CS)	Eq. (4) (G)	Eq. (5) (HR)	Flory's theory Eq. (7)
Toluene + <i>n</i> -heptane + <i>n</i> -hexane	19.57	-9.30	11.77	31.62	-11.23	-0.66
Cyclohexane + <i>n</i> -heptane + <i>n</i> -hexane	22.87	-3.77	15.67	34.15	-4.43	0.88
<i>n</i> -Hexane + <i>n</i> -heptane + <i>n</i> -decane	18.21	-10.90	10.42	30.36	-12.31	7.99

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