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Estimation of Some Important Thermodynamic Properties of Organic Liquid Mixtures from Ultrasonic Velocity and Density Data

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Abstract

Using the recently proposed equations for calculating thermal expansion coefficient (α) and isothermal compressibility (β_T) from density (ρ) and ultrasonic velocity (u) values, six binary organic liquid mixtures have been considered. These are: n-heptane+toluene (I); n-heptane+n-hexane (II); toluene+n-hexane (III); cyclohexane+n-heptane (IV); cyclohexane+n-hexane (V), and n-decane+n-hexane (VI) at 298.15 K. Literature data for ρ and u of these mixtures are employed to compute α, β_T, as well as γ, P_{int} and Γ. Calculated values of β_T are compared with the earlier ones, and the agreement is found to be good.

Keywords: Isothermal compressibility; Thermodynamic properties; Ultrasonic velocity; Organic liquid mixtures

Introduction

Estimation of thermodynamic properties through empirical modeling have immense applications in industry, pollution control, oil recovery and separation processes. The measurements of ultrasonic velocity and density data of liquid and liquid mixtures provide very simple method for estimating a number of useful and important thermodynamic properties e.g. adiabatic compressibility, intermolecular free length, free volume, acoustic impedence, relative association, relaxation time etc. Such studies have been carried out by several workers [1-13]. On the other hand, various statistical mechanical theories [14-17] (Flory theory, hole theory, hard sphere equations of state etc.) have been employed to compute theoretically the ultrasonic velocity, density, excess volume, excess adiabatic compressibility, internal pressure, solubility parameter, non-linearity parameter, guineisen parameter etc. of liquid mixtures. However, thermal expansivity and isothermal compressibility and their related properties (heat capacities ratio, internal pressure etc.) have not been calculated from ultrasonic velocity (u) and density (ρ) values. Recently [16,18,19], two empirical relations based on dimensional analysis were obtained showing the direct relations between thermal expansion coefficients (α) and isothermal compressibility (β_T) with ultrasonic velocity (u) and density (ρ). In the present communication we have applied these relations for the estimation of thermal expansivity (α), isothermal compressibility (β_T), internal pressure (P_{int}), heat capacity ratio (γ) and pseudo guineisen parameter (Γ) of binary organic liquid mixtures. The experimental data of ρ and u for these binary mixtures have been taken from literature (20).

Formula Used

α and β_T of a liquid system is related to *ρ and u* by the following expressions:

$$\alpha = \frac{75.6\times10^{-3}}{T^{1/9}U^{1/2}\rho^{1/3}} \quad \gamma = \frac{C_P}{C_V} = \frac{\beta_T}{\beta_S} \tag{1}$$

$$\beta_T = \left(\frac{1.71\times10^{-3}}{T^{4/9}U^{2}\rho^{4/3}}\right) \tag{2}$$

where all the symbols have their usual meanings. The internal pressure, P_{int}, of liquid is given by

$$P_{int} = \frac{\alpha_T}{\beta_T} - P \tag{3}$$

where P is the external pressure when P = 0, he above equations becomes

$$P_{int} = \frac{\alpha_T}{\beta_T} \tag{4}$$

Substituting the values of α, β_T from eqs (1) and (2) into above equation, we get

$$P_{int} = 44.2\times T^{4/3}u^{3/2}\rho \tag{5}$$

The heat capacity ratio $\gamma = \frac{C_P}{C_V} = \frac{\beta_T}{\beta_S}$ (6)

Where C_p and C_v are respectively the heat capacities at constant pressure and at constant volume, β_s is the isentropic compressibility, defined by

$$\beta_S = (u^2\rho)^{-1} \tag{7}$$

Combining eqs (2), (6) and (7), we gets

$$\gamma = \frac{17.1\times10^{-3}}{T^{4/9}\cdot\rho^{1/3}} \tag{8}$$

The value of pseudo-guineisen parameter, Γ is given by

$$\Gamma = \frac{\gamma - 1}{\alpha T} \tag{9}$$

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Obtaining the values α, from eq. (1) and γ from eq. (8), we have computed the value of Γ from eq. (9).

Results and Discussion

The method utilized in the present paper is easy to implement on variety of simple and complex fluid systems comparatively recently proposed methods based on various version of SAFT (Statistical associating fluid theory for variable range interactions (SAFT-VR) of the generic Mie form, SAFT+cubic and Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT). For the calculations of α, β_T and other thermodynamic properties from eq^s (1) to (9) we, have considered the following binary organic liquid mixtures:

(I) n-heptane(x_1)+toluene(x_2)

(II) n-heptane(x_1)+n-hexane(x_2)

(III) n-hexane(x_2)+toluene(x_1)

(IV) n-heptane(x_2)+cyclohexane (x_1)

(V) n-hexane(x_2)+cyclohexane(x_1)

(VI) n-hexane(x2)+n-decane(x1)Ultrasonic and density measurement of these systems were carried out by Pandey et al. [16-19] at 298.15 K. These data have been taken for the present calculation Table 1. Calculated values of α, β_T, P_{int},

Similarly computed values of these properties for the systems (I) to (VI) are presented respectively in Tables 2-7. For each binary mixture, the percentage and average percentage deviation for the β_T values are given. Since the experimental values of β_T are known, only deviation in β_T values was calculated. Calculations of β_T for the afro said organic liquid mixture [20, 21] and also other mixtures have been carried out on the basis of various hard sphere models and Flory's statistical theory.

Unfortunately, in both the papers there is controversy about the experimental values of β_T which have been used to compare the theoretical results. In one case authors [21] considered the β_T values obtained from Flory theory as the experimental ones which is not justified. In the second case, authors [20] employed purely empirical relation (combination of Auerbach and Mc Gowan) for the experimental β_T values which is absurd. A perusal of Tables 2-7 shows that the average percentage deviations of the calculated β_T values for mixtures (I) to (VI) are respectively 7.04 and 12.97, 7.69, 9.80, 10.79 and 11.89. Keeping in view the uncertainties in the experimental β_T values employed, our agreement is quite good, and far better than the earlier results.

The values of internal pressures are increasing with increasing mole fraction for the systems II, III, IV, V and VI. This decrease in P_{int} values may be attributed to the existence of columbic forces in the mixture [22]. In case of system I, the behavior is opposite due to lack of columbic forces. β_T values are also increasing for all the systems except system- I. In system-I, intermolecular forces are strong due to the presence of π electrons. Similar observation was observed in case of thermal expansion coefficients [23,24] For system –I, α values

298.15 K [Experimental]			
Component	**V**	**α x 10^3 (deg^{-1})**	**βT x 10^{12} (cm^2 $dyne^{-1}$)**
Toluene	106.87	1.086	142.40
n-Heptane	147.47	1.258	112.40
Cyclohexane	108.76	1.215	112.77
n-Hexane	131.56	1.381	166.90
n-Decane	195.94	1.050	116.30

ϒ and Γ of all the pure components are recorded in Table 1

298.15 K [Calculated]					
Component	**α x 10^3 (deg^{-1})**	**βT x 10^{12} (cm^2 $dyne^{-1}$)**	**P_{int} x 10^{-9} (dyne cm^{-2})**	**γ**	**Γ**
Toluene	1.167	9729.2	3.322	1.427	1.226
Cyclohexane	1.235	122.0	3.021	1.480	1.302
n-Hexane	1.409	206.5	2.034	1.565	1.344
n-Heptane	1.357	178.0	2.273	1.546	1.348
n-Decane	1.331	164.5	2.411	1.512	1.289

List of abbreviations used in Tables:
x: Mole fraction
ρ: Density
u: Ultrasonic velocity
α: Thermal expansion coefficient
β_T: Isothermal compressibility
P_{int}: Internal pressure
γ: heat capacity ratio
Γ: Pseudo gruneisen parameter

Table 1: Experimental and calculated values of α, βT, Pint, γ and Γ for pure components at 298.15 K

(x_1)	α x 10^3 (deg^{-1})	βT x 10^{12} (cm^2 $dyne^{-1}$)	Pint x 10^{-9} (dyne cm^{-2})	γ	Γ	%D β_T
0.2979	1.190	105.2	3.371	1.424	1.195	6.32
0.3162	1.194	106.4	3.343	1.425	1.193	6.31
0.3325	1.196	107.3	3.322	1.427	1.197	6.41
0.3519	1.200	108.5	3.295	1.429	1.199	6.54
0.3709	1.203	109.7	3.267	1.431	1.201	6.68
0.3902	1.206	111.0	3.240	1.432	1.201	6.86
0.4029	1.199	111.9	3.220	1.434	1.214	6.90
0.4282	1.212	113.2	3.192	1.436	1.206	7.03
0.4484	1.206	114.6	3.163	1.438	1.218	7.18
0.4684	1.210	116.0	3.133	1.440	1.219	7.32
0.4874	1.222	117.0	3.135	1.442	1.213	7.42
0.5023	1.231	120.2	3.051	1.450	1.226	7.73
0.5227	1.225	121.8	3.020	1.452	1.237	6.47
0.5442	1.238	123.1	2.997	1.457	1.238	8.00
0.5446	1.242	124.7	2.968	1.456	1.231	8.15

Average percent deviation =7.04
List of abbreviations used in Table
x: Mole fraction
ρ: Density
u: Ultrasonic velocity
α: Thermal expansion coefficient
β_T: Isothermal compressibility
P_{int}: Internal pressure
γ: heat capacity ratio
Γ: Pseudo gruneisen parameter

Table 2: Calculated values of α, βT, Pint, γ and Γ of binary system— n-heptane(x1) + toluene at 298.15 K.

(x_1)	α x 10^3 (deg^{-1})	β_T x 10^{12} (cm^2 $dyne^{-1}$)	P_{int} x 10^{-9} (dyne cm^{-2})	γ	Γ	%D β_T
0.3388	1.394	198.1	2.098	1.559	1.344	13.31
0.3598	1.393	197.1	2.106	1.558	1.343	13.26
0.3782	1.393	197.4	2.104	1.560	1.348	13.27
0.4001	1.390	195.9	2.116	1.557	1.344	12.35
0.4193	1.390	195.7	2.117	1.558	1.346	13.18
0.4394	1.389	194.9	2.124	1.557	1.344	13.13
0.4604	1.388	194.3	2.129	1.556	1.343	13.10
0.4782	1.386	193.5	2.135	1.556	1.345	13.05
0.4986	1.385	192.7	2.141	1.555	1.344	13.02
0.5191	1.383	191.6	2.151	1.554	1.343	12.95
0.5395	1.381	190.8	2.157	1.553	1.304	12.90
0.5594	1.378	189.1	2.173	1.550	1.338	12.81
0.5795	1.378	189.2	2.171	1.551	1.341	12.82
0.6025	1.377	188.5	2.178	1.550	1.339	12.77
0.6185	1.376	188.1	2.181	1.550	1.340	12.75

Average percent deviation =12.97
List of abbreviations used in Tables:
x: Mole fraction
ρ: Density
u: Ultrasonic velocity
α: Thermal expansion coefficient
β_T: Isothermal compressibility
P_{int}: Internal pressure
γ: heat capacity ratio
Γ: Pseudo gruneisen parameter

Table 3: Calculated values of α, βT, Pint, γ and Γ of binary system— n-heptane(x1) + n-hexane at 298.15 K.

(x_1)	α x 10^3 (deg^{-1})	β_T x 10^{12} (cm^2 $dyne^{-1}$)	P_{int} x 10^{-9} (dyne cm^{-2})	γ	Γ	%D βT
0.4074	1.278	139.9	2.723	1.467	1.225	9.46
0.4299	1.274	137.9	2.752	1.465	1.224	9.30
0.4486	1.268	135.7	2.787	1.459	1.214	9.11
0.4704	1.264	133.9	2.814	1.460	1.220	8.97
0.4919	1.259	131.9	2.846	1.457	1.217	8.80
0.5114	1.254	129.8	2.881	1.454	1.214	8.60
0.5290	1.251	128.2	2.907	1.452	1.211	8.47
0.5491	1.243	125.2	2.960	1.446	1.203	6.78
0.5584	1.232	124.9	2.965	1.447	1.207	7.98
0.5880	1.242	123.0	3.000	1.444	1.202	6.53
0.6088	1.238	120.8	3.039	1.442	1.203	6.18
0.6275	1.232	119.2	3.070	1.440	1.197	6.85
0.6453	1.211	116.2	3.129	1.434	1.196	4.97
0.6637	1.217	115.1	3.152	1.433	1.193	6.30
0.6829	1.204	114.0	3.175	1.436	1.203	7.12

Average percent deviation =7.69
List of abbreviations used in Tables:
x: Mole fraction
ρ: Density
u: Ultrasonic velocity
α: Thermal expansion coefficient
β_T: Isothermal compressibility
P_{int}: Internal pressure
γ: heat capacity ratio
Γ: Pseudo gruneisen parameter

Table 4: Calculated values of α, βT, Pint, γ and Γ of binary system— toluene(x1) + n-hexane at 298.15 K.

(x_1)	α x 10^3 (deg^{-1})	β_T x 10^{12} (cm^2 $dyne^{-}$)	P_{int} x 10^{-9} (dyne cm^{-2})	γ	Γ	%D β_T
0.2227	1.318	158.0	2.485	1.517	1.315	10.83
0.2689	1.312	155.5	2.515	1.522	1.334	10.65
0.3158	1.623	153.4	2.542	1.513	1.060	10.50
0.3588	1.308	153.6	2.539	1.516	1.323	10.51
0.4016	1.305	150.7	2.575	1.513	1.318	10.30
0.4433	1.296	147.8	2.614	1.508	1.314	10.08
0.4861	1.291	145.6	2.643	1.507	1.317	9.94
0.5270	1.287	143.9	2.666	1.505	1.316	9.78
0.5642	1.284	142.3	2.688	1.503	1.313	9.65
0.6019	1.279	140.4	2.716	1.501	1.313	9.50
0.6414	1.275	138.7	2.741	1.500	1.315	9.36
0.6795	1.271	136.9	2.767	1.498	1.314	9.22
0.7164	1.268	135.3	2.792	1.497	1.314	9.08
0.7521	1.263	133.5	2.820	1.494	1.317	8.93
0.7877	1.260	132.0	2.845	1.491	1.307	8.80

Average percent deviation = 9.80
List of abbreviations used in Tables:
x: Mole fraction
ρ: Density
u: Ultrasonic velocity
α: Thermal expansion coefficient
β_T: Isothermal compressibility
P_{int}: Internal pressure
γ: heat capacity ratio
Γ: Pseudo gruneisen parameter

Table 5: Calculated values of α, β_T, P_{int}, γ and Γ of binary system- cyclohexane(x1) + n-heptane at 298.15 K.

(x_1)	α x 10^3 (deg^{-1})	βT x 10^{12} ($cm2\ dyne^{-1}$)	P_{int} x 10^{-9} (dyne cm^{-2})	γ	Γ	%D βT
0.2189	1.368	183.7	2.220	1.543	1.331	12.51
0.2541	1.354	179.4	2.260	1.541	1.340	12.23
0.2981	1.347	172.5	2.364	1.536	1.334	11.80
0.3150	1.346	171.9	2.333	1.535	1.333	11.77
0.3647	1.338	167.9	2.375	1.531	1.331	11.50
0.3897	1.331	164.7	2.410	1.529	1.333	11.28
0.4258	1.325	161.7	2.442	1.525	1.328	11.09
0.4777	1.317	157.7	2.489	1.521	1.326	10.81
0.5029	1.311	155.0	2.522	1.519	1.327	10.65
0.5675	1.301	150.2	2.581	1.514	1.325	10.26
0.5799	1.299	149.1	2.596	1.512	1.321	10.18
0.6012	1.294	146.9	2.625	1.511	1.324	10.01
0.6695	1.283	142.1	2.692	1.505	1.320	9.51
0.7187	1.274	138.1	2.749	1.501	1.318	9.32
0.7888	1.264	133.6	2.819	1.495	1.313	8.94

Average percent deviation = 10.79
List of abbreviations used in Tables:
x: Mole fraction
ρ: Density
u: Ultrasonic velocity
α: Thermal expansion coefficient
β_T: Isothermal compressibility
P_{int}: Internal pressure
γ: heat capacity ratio
Γ: Pseudo gruneisen parameter

Table 6: Calculated values of α, β_T, P_{int}, γ and Γ of binary system-cyclohexane(x1) + n-hexane at 298.15 K.

(x_1)	α x 10^3 (deg^{-1})	β_T x 10^{12} ($cm^2\ dyne^{-1}$)	P_{int} x10^{-9} (dyne cm^{-2})	γ	Γ	%D βT
0.0187	1.401	201.8	2.068	1.556	1.331	13.52
0.0588	1.396	198.8	2.092	1.553	1.328	13.35
0.1008	1.388	194.7	2.126	1.550	1.329	13.13
0.1436	1.381	190.6	2.169	1.547	1.328	12.90
0.1896	1.377	188.6	2.176	1.547	1.332	12.78
0.2348	1.367	183.2	2.225	1.541	1.327	12.46
0.2886	1.359	178.6	2.267	1.539	1.330	12.18
0.3350	1.351	174.7	2.305	1.536	1.330	11.99
0.3872	1.345	171.4	2.338	1.534	1.325	11.73
0.4449	1.338	167.8	2.376	1.531	1.331	11.50
0.5009	1.333	164.3	2.414	1.529	1.333	11.26
0.5627	1.321	159.8	2.465	1.525	1.332	10.95
0.6248	1.313	155.7	2.513	1.523	1.335	10.66
0.6944	1.306	152.6	2.551	1.522	1.340	10.43
0.7655	1.298	149.7	2.600	1.520	1.343	9.65

Average percent deviation = 11.89
List of abbreviations used in Tables:
x: Mole fraction
ρ: Density
u: Ultrasonic velocity
α: Thermal expansion coefficient
β_T: Isothermal compressibility
P_{int}: Internal pressure
γ: heat capacity ratio
Γ: Pseudo gruneisen parameter

Table 7: Calculated values of α, β_T, P_{int}, γ and Γ of binary system- n-decane(x1) + n-hexane at 298.15 K.

are increasing with the mole fraction of component I which may be interpreted in terms of closure approach of unlike molecules [25]. ϒ values are found to follow the general trend.

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