



Estimation of internal pressure and pseudo-gruneisen parameter of binary liquid mixtures from 288.15-318.15K

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Abstract

From the knowledge of thermal expansion coefficient (α) and isothermal compressibility (β_T), various thermodynamic properties were analyzed from the experimental values of density and acoustical parameters for different binary liquid mixtures. In present investigation, mixtures of isomeric alcohols with saturated hydrocarbon at different temperatures over the whole range of mole fraction and one atmospheric pressure were used to determine the theoretical values of internal pressure (P_i), pseudo-gruneisen parameter (Γ) and their excess values. Flory's statistical theory, Ramaswamy model and model proposed by Glinski were used to determine the aforesaid properties and analyze the behaviour of liquid mixtures in terms of the interaction forces acting between the components. Absolute average percent deviation (AAPD) was considered as the criterion for the success of results. Experimental values of properties were utilized to determine the numerical coefficients (A_i) and standard deviation (δ) by redlich-kister equation. Excess values (Γ^E) were used to analyze the interactions present between the components of liquids at different temperatures. Non-associated model deals fair agreement in comparison to associated models except few points.

Keywords: Internal pressure, gruneisen parameter, binary systems, statistical theory, butanol.

Introduction

In past few years researchers¹⁻³ have focused on the theoretical evaluation of ultrasonic velocity, isotropic compressibility, excess volume, surface tension and viscosity of liquid mixtures to interpret the intermolecular association between the binary constituents of liquids. In recent past, the usefulness of Pseudo-Gruneisen parameter is explored in the characterization of solid crystalline lattice⁴. Several researchers⁵⁻⁸ have made a Pioneer attempt to study the significance of these thermodynamic properties and its correlation with other properties. Hildebrand⁹ proposed the concept to analyze the overall effect of internal pressure in the thermodynamics of solute-solvent interactions. It effectively works in the quantitative study of intermolecular forces. Internal pressure can also be computed indirectly with the help procedure advised by Suryanarayan¹⁰. In liquids a small volume expansion at constant temperature, components have to do work against the cohesive forces acting between them. This is responsible for change in internal energy (E).

A small change in internal energy with respect to small volume expansion under isothermal condition is called internal pressure, $(\partial E/\partial V)_T$. In case of aprotic organic liquids $(\partial E/\partial V)_T = m n \Delta E_{\text{vap}}/V_m$, where, ΔE_{vap} is called as vaporisation energy and V_m is the molar volume. Pseudo-Gruneisen parameter plays a significant role to define concept of anharmonicity of solid crystalline lattice. It is effectively used in the determination of internal structures and quasi crystalline properties of liquids, liquid metal alloys and higher saturated

hydrocarbons. Generally liquid supports the quasi crystalline model. Lattice nature of quasi crystalline state is mainly affected by temperature and pressure. In the continuation of previously published work¹¹⁻¹⁴, this paper is deals with the theoretical estimation of internal pressure, pseudo-gruneisen parameter and excess values for weakly interacting liquids at different temperatures. To carry out such investigation the aforementioned properties were computed from the experimental values of densities and ultrasonic velocities obtained for the mixture of 1-butanol and 2-butanol with dodecane from 288.15- 318.15K temperature and one atmospheric pressure over the entire range of mole fraction. Experimental and literature values¹⁵ of density and ultrasonic speed for pure liquids are compared in Table-1. These values were compared with the computed values obtained from Flory¹⁶⁻²⁰ theory, Ramaswamy-Anbananthan model²¹ and model proposed by Glinski²² based on non-association and association process respectively.

The theoretical values of discussed parameters obtained from experimental analysis were utilized in regression based redlich-kister polynomial²³ to determine the coefficients and their respective standard error. Excess values of pseudo-gruneisen parameters for the concerned mixtures were also evaluated to analyze the interactions between the components of liquids at different temperatures. The main aim of this investigation is to analyze the interactions involved in liquid components and verify applicability as well as the accuracy of aforementioned models at various temperatures.

Table-1: Experimental and literature values of thermodynamic properties pure liquids.

Liquids	T/K	$\alpha \times 10^3$	$\beta_T \times 10^{12}$	V	$\rho_{\text{exp}}^{(14)}$	$\rho_{\text{lit}}^{(14)}$	$U_{\text{exp}}^{(14)}$	$U_{\text{lit}}^{(14)}$
		K ⁻¹	Pa	cm ³ mol ⁻¹	g.cm ⁻³	g.cm ⁻³	ms ⁻¹	ms ⁻¹
1-Butanol	288.15	1.2886	112.04	91.12	0.8135	0.8133	1273.51	-
	298.15	1.3111	118.00	91.98	0.8059	0.8057	1239.29	-
	308.15	1.3348	124.50	92.88	0.7980	0.7980	1205.5	1203
	318.15	1.3596	131.59	93.82	0.7901	0.7901	1172.12	-
2-Butanol	288.15	1.3091	117.47	91.48	0.8103	-	1247.03	-
	298.15	1.3342	124.34	92.40	0.8022	0.8026	1210.98	1212
	308.15	1.3614	132.10	93.38	0.7038	0.7939	1174.53	-
	318.15	1.3911	140.93	94.44	0.7849	0.7849	1137.61	-
Dodecane	288.15	1.3044	116.21	226.40	0.7524	0.7526	1317.27	-
	298.15	1.3298	123.13	228.59	0.7452	0.7453	1278.2	1278
	308.15	1.3564	130.66	230.82	0.7380	0.7380	1239.82	-
	318.15	1.3843	138.89	233.12	0.7307	0.7307	1201.88	-

Computational and theoretical analysis

Prigogine–Flory–Patterson Theory: Prigogine –Flory-Patterson¹⁶⁻²⁰ model is based on non-associated process developed for Y-meric non-electrolytic spherical type chain molecules having weakly interacting and associating properties. With the help of thermodynamic parameter such as (α), (β_T) characteristic properties (P^*), (T^*), (V^*) as well as reduced properties (\tilde{V}), (\tilde{T}) can be obtained. Flory determines these parameters from the given equation of state as;

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{1/3}}{\tilde{V}^{1/3}-1} - \frac{1}{\tilde{V}\tilde{T}} \quad (1)$$

$$\tilde{P} = \frac{P}{P^*}, \tilde{T} = \frac{T}{T^*}, \tilde{V} = \frac{V}{V^*} \quad (2)$$

$$\alpha_{\text{Flory}} = \frac{3(\tilde{V}^{1/3}-1)}{\tilde{T}(1-3(\tilde{V}^{1/3}-1))} \quad (3)$$

β_T values can be obtained by the given relation as;

$$\beta_{T,\text{Flory}} = \frac{\alpha_T \tilde{V}}{P^*} \quad (4)$$

P_i values can be obtained by the given relation as;

$$P_{i,\text{Flory}} = \tilde{T} \cdot \gamma_P \quad (5)$$

Where, γ_P is termed as thermal expansion coefficient and it is obtained by;

$$\gamma_P = \frac{P^*}{T\tilde{V}^2} \quad (6)$$

For experimental internal pressure, γ_P is computed by the relation as;

$$\gamma_P = \frac{\alpha_{\text{exp}}}{\beta_{T,\text{exp}}} \quad (7)$$

Pseudo-gruneisen values for liquid mixture are obtained as;

$$\Gamma_{\text{Flory}} = \frac{U^2 \alpha}{C_P} \quad (8)$$

C_P value in above equation (8) can be determined by the relation as under;

$$C_{P,\text{Mix}} = C_P^E + C_P^{\text{Ideal}} \quad (9)$$

$$C_P^{\text{Ideal}} = \sum_{i=1}^2 x_i C_{P,i} \quad (10)$$

$$C_P^E = \frac{P^* V^*}{T^*} \left[\frac{1}{\left(\frac{4}{3}\right)\tilde{V}_i^{-1/3}-1} - \sum \left\{ \frac{x_i}{\left(\frac{4}{3}\right)\tilde{V}_i^{-1/3}-1} \right\} \right] \quad (11)$$

Ramaswamy- Anbananthan model: Ramaswamy²¹ proposed a model to describe molecular interactions between the components using a linear relation of acoustic impedance with the mole fractions of binary components. According to them, when two liquids $A_{Li q (1)}$ and $B_{Li q (2)}$ are mixed to each other then associate $AB_{Li q (12)}$ will be formed by the equation as;



Association constant (K_{as}) can be determined by given relation;

$$K_{as} = \frac{[AB_{Li q (12)}]}{[A_{Li q (1)}][B_{Li q (2)}]} \quad (13)$$

Now apply this concept for desired properties;

$$P_{iTheo} = X_{Li q (1)}P_{iLi q (1)} + X_{Li q (2)}P_{iLi q (2)} \quad (14)$$

Where, $X_{Li q (1)}$, $X_{Li q (2)}$, $P_{iLi q (1)}$ and $P_{iLi q (2)}$ are the mole fractions and internal pressure of pure liquid and their associate AB respectively. Equation (14) can be modified into Equation (15) due to the presence of non-reacted components with the associates at concentrated solution.

$$P_{iTheo} = X_{Li q (1)}P_{iLi q (1)} + X_{Li q (2)}P_{iLi q (2)} + X_{Li q (12)}P_{iLi q (12)} \quad (15)$$

Associated model can be represented as;

$$K_{as} = \frac{[AB_{Li q (12)}]}{(C_{A_{Li q (1)}} - [AB_{Li q (12)}])(C_{B_{Li q (2)}} - [AB_{Li q (12)}])} \quad (16)$$

In theoretical analysis, values of internal pressure was determined by substituting the hypothetical values of associated component $AB_{Li q (12)}$ and association constant (K_{as}) as adjustable parameter for desired property to get minimum deviation from the experimental values. Sum of square of deviation for observed and theoretically estimated properties can be determined as;

$$S = \sum (P_{iobs} - P_{iTheo})^2 \quad (17)$$

Where, P_{iobs} and P_{iTheo} are observed and calculated internal pressure respectively.

Model revised by Glinski: Glinski²² has given a revised relation based on the concept of additively with volume fractions (ϕ) for various thermo-physical properties. In this proposed work the model is applied to determine the P_i as well as Γ values by the relation given below;

$$P_{iTheo} = \frac{P_A P_B P_{AB}}{\phi_A P_B P_{AB} + \phi_{AB} P_A P_B + \phi_B P_A P_{AB}} \quad (18)$$

Where: ϕ_A and ϕ_B are volume fraction of liquid component A and B respectively. Theoretical evaluation of association constant, K_{as} for both the models are very much similar.

Results and Discussion

Ramaswamy- Anbananthan based on association process deals with the linear relation between acoustical parameter (Z) with the mole fraction (X_i) of the components have been already checked by us in our previously published work to predict the associational behaviour. Such process usually related to deviation of different properties from additivity.

In our previously published work, various ultrasonic, thermodynamic and transport properties were analyzed by Ramaswamy and model devised by Glinski. Estimation of aforementioned parameters at different temperature analyze the molecular interactions in liquid mixture is our first attempt. The theoretical values for such models were computed from the computer programme, we constructed a data sheet with association constant K_{as} and fitted parameter, P_{AB} for internal pressure of associate. Theoretical values discussed parameters can be obtained by changing the fitted values manually. The observed values of these parameters were obtained from the following empirical relations:

$$\alpha_{exp} = \frac{75.6 \times 10^{-3}}{T^{1/9} U^{1/2} \rho^{1/3}} K^{-1} \quad (19)$$

$$\beta_{T(exp)} = \frac{1.17 \times 10^{-3}}{T^{4/9} \rho^{4/3} U^2} \text{ cm}^2 \text{ dyne}^{-1} \quad (20)$$

For pure liquids the experimental values of thermal expansion coefficient (α), isothermal compressibility (β_T) at different temperatures are recorded in Table-1.

Thermal expansion coefficient is a very interesting as well as sensitive thermodynamic parameter affected largely by small change in temperature. Numerical values of coefficient computed from Redlich-Kister polynomial²³ and their respective S.D. (δ) values are reported in Table-2. S.D. (δ) values for both the binary system varies from (0.007-0.092) and (0.472-0.582) at aforementioned temperatures respectively.

$$\Delta P_i = X_i(1 - X_i) \sum_{i=0}^n A_i(1 - X_i)^i \quad (21)$$

In above equation; ΔP_i = Deviation in internal pressure. X_i = mole fraction, A_i = coefficient. The values of coefficients (A_i) were computed from by least square method.

S.D (δ) value can be calculated by the expression given below;

$$S.D(\delta) = \left[\left(\sum_{i=1}^n \frac{(P_{i,exp} - P_{i,theo})^2}{(E.P - A.P)} \right)^{1/2} \right] \quad (22)$$

Where: δ = Standard deviation, E.P. = Number of experimental points, A.P. = Number of adjustable parameters.

Table-2: Coefficients and Standard deviation (δ) of redlich-kister equation.

	T/K	A ₀	A ₁	A ₂	A ₃	(δ)
1-Butanol+ Dodecane ΔP_i	288.15	0.079	-0.383	1.647	1.544	0.081
	298.15	-0.292	-0.064	-0.392	0.694	0.007
	308.15	-0.661	0.245	-2.371	-0.153	0.035
	318.15	-1.015	0.544	-4.282	-0.992	0.092
2-Butanol+ Dodecane ΔP_i	288.15	2.087	-2.545	33.742	40.077	0.582
	298.15	1.813	-2.728	30.872	40.313	0.546
	308.15	1.550	-2.878	27.945	40.326	0.509
	318.15	1.301	-2.986	24.994	40.094	0.472

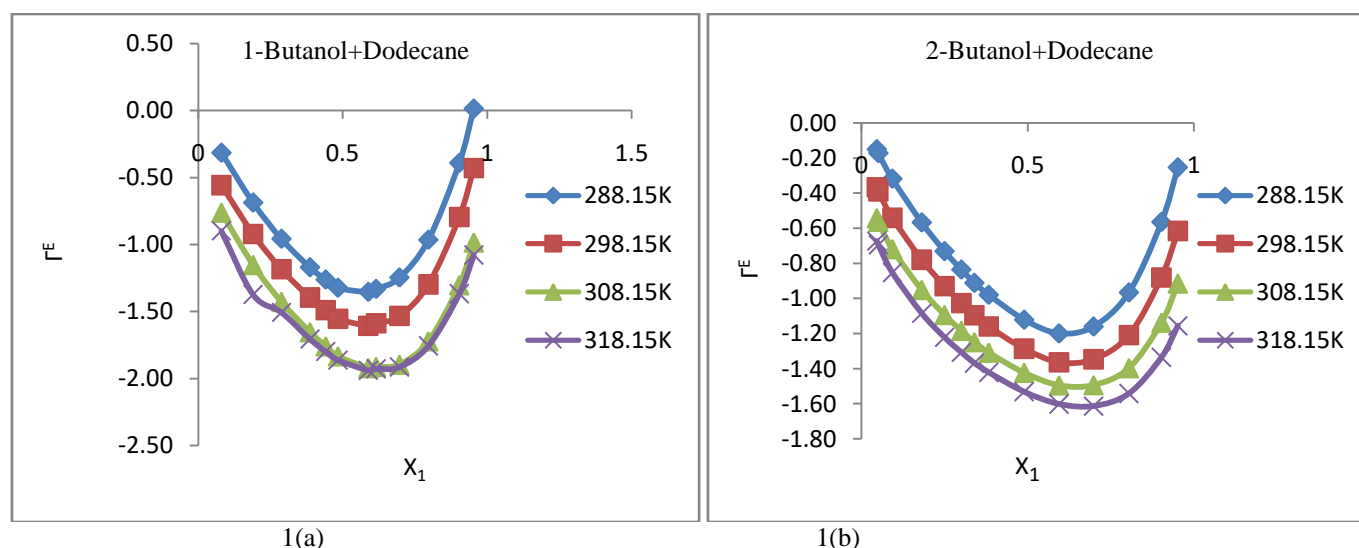


Figure-1: Plot of variation of observed excess pseudo Gruneisen parameter versus mole fraction at different temperatures.

Table-3: AAPD values of thermo physical properties at different temperatures.

T/K	K _{as}	F _{lory}	Γ _{RS}	Γ _{Gli}	Pi _{Flory}	Pi _{RS}	Pi _{Gli}
1-Butanol+ Dodecane							
288.15	0.001	3.29	6.48	2.63	2.55	1.89	1.86
298.15	0.001	2.42	10.54	7.24	1.44	2.18	2.20
308.15	0.001	11.43	16.97	13.54	5.67	6.49	6.51
318.15	0.001	20.77	21.27	18.53	10.17	11.08	11.09
2-Butanol+ Dodecane							
288.15	0.001	5.39	9.55	3.94	0.86	1.06	1.08
298.15	0.001	3.61	14.01	8.93	5.01	5.12	5.16
308.15	0.001	12.77	18.71	14.12	9.91	10.00	10.04
318.15	0.001	22.61	23.60	19.44	15.15	15.19	15.23

The results of AAPD for internal pressure and pseudo-gruneisen parameter obtained from the aforementioned models from 288.15-318.15K are reported in Table-3 and Table-4 consist of experimental theoretical results of aforesaid properties at different temperatures. A deep insight of Table-3 indicate that

the values of AAPD increases with increase in temperature for both the binary system except for 1-Butanol+Dodecane at 298.15K. A very close observation of Table 4 clearly indicate that experiential and theoretical values of internal pressure as well as excess pseudo-gruneisen parameter computed for the discussed models increases but decreases with increase in temperatures. Similar trends are observed for both the system. Sign and magnitude of excess properties are essential criteria for describing the molecular interaction involved in the liquid system. Γ^E with negative values represent of strong molecular associations between the components. Structural effects and dispersion forces arising from interstitial accommodation of liquid components contribute negative term to Γ^E . Similar trends and non-linear variations are observed for excess pseudo-gruneisen parameter at different temperatures as shown in Figure-1(a) and 1(b), indicating molecular interactions between the binary components. At temperature 308.15 and 318.15K,

molecular interactions are almost similar over the entire mole fractions except few points. Statistical model of Flory deals a fair agreement as compared to Ramaswamy and Glinski models. Small deviation results obtained from PFP model is due to the fact that the model was developed for Y-meric non-electrolytic spherical type chain molecules and systems taken for analysis consist of weak association and interactions. Positive trends of Γ^E suggest the weak molecular interaction due to electronic repulsion between non bonded electrons of binary components and favour the packing of unlike molecules.

$$\Gamma^E = \Gamma_{\text{Mix}} - (X_1\Gamma_1 + X_2\Gamma_2) \quad (23)$$

In above equation Γ_{Mix} is pseudo-gruneisen parameter of liquid mixture and Γ^E is excess pseudo-gruneisen parameter.

Table-4: Experimental and theoretical values of thermodynamic properties and their excess functions at different temperatures.

X_1	$\rho_{\text{exp}}/\text{g.cm}^{-3}$	U_{exp}	Pi_{obs}	Pi_{Flory}	Pi_{RS}	Pi_{Gli}	Γ_{obs}^E	Γ_{Flory}^E	Γ_{RS}^E	Γ_{Gli}^E
1-Butanol+ Dodecane. At 288.15k										
0.08048	0.7538	1311.88	3.297	3.235	3.241	3.242	-0.316	-0.169	-0.001	-0.239
0.19017	0.7565	1306.67	3.301	3.237	3.249	3.252	-0.688	-0.456	-0.001	-0.528
0.28812	0.7595	1302.34	3.306	3.239	3.257	3.261	-0.959	-0.672	-0.002	-0.744
0.38654	0.7630	1298.07	3.312	3.242	3.265	3.269	-1.171	-0.841	-0.002	-0.913
0.44097	0.7652	1295.76	3.317	3.244	3.269	3.274	-1.263	-0.911	-0.002	-0.982
0.4835	0.7671	1293.98	3.321	3.245	3.272	3.278	-1.324	-0.952	-0.002	-1.025
0.58849	0.7727	1289.78	3.333	3.251	3.281	3.286	-1.355	-0.997	-0.002	-1.067
0.61515	0.7743	1288.69	3.337	3.253	3.283	3.288	-1.333	-0.994	-0.002	-1.063
0.69605	0.7796	1285.21	3.350	3.260	3.289	3.294	-1.248	-0.940	-0.002	-1.009
0.79594	0.7878	1280.87	3.372	3.271	3.297	3.301	-0.966	-0.768	-0.002	-0.840
0.90295	0.7991	1276.41	3.406	3.289	3.306	3.308	-0.391	-0.422	-0.001	-0.498
0.95321	0.8057	1274.76	3.427	3.301	3.310	3.311	0.014	-0.197	0.000	-0.266
0.08048	0.7465	1272.60	3.150	3.221	3.227	3.242	-0.557	-0.529	-0.001	-0.213
0.19017	0.7491	1267.38	3.155	3.222	3.237	3.252	-0.922	-0.805	-0.001	-0.469
0.28812	0.7520	1263.17	3.161	3.224	3.246	3.261	-1.186	-1.018	-0.002	-0.659
0.38654	0.7555	1259.03	3.169	3.227	3.255	3.269	-1.397	-1.191	-0.002	-0.808
0.44097	0.7577	1256.85	3.174	3.231	3.260	3.274	-1.492	-1.267	-0.002	-0.869

0.4835	0.7596	1255.23	3.179	3.233	3.264	3.278	-1.555	-1.315	-0.002	-0.905
0.58849	0.7651	1251.40	3.193	3.235	3.274	3.286	-1.608	-1.387	-0.002	-0.940
0.61515	0.7667	1250.47	3.197	3.242	3.276	3.288	-1.589	-1.394	-0.002	-0.937
0.69605	0.7720	1247.52	3.212	3.245	3.284	3.294	-1.535	-1.377	-0.002	-0.888
0.79594	0.7802	1244.06	3.237	3.252	3.293	3.301	-1.298	-1.271	-0.001	-0.736
0.90295	0.7916	1240.79	3.273	3.265	3.303	3.308	-0.795	-1.026	-0.001	-0.435
0.95321	0.7982	1239.77	3.296	3.285	3.308	3.311	-0.430	-0.861	0.000	-0.232
At 308.15k										
0.08048	0.7391	1228.72	3.002	3.200	3.207	3.209	-0.762	-0.292	-0.199	-0.199
0.19017	0.7417	1227.03	3.007	3.202	3.218	3.221	-1.152	-0.537	-0.439	-0.439
0.28812	0.7445	1225.05	3.014	3.206	3.229	3.232	-1.428	-0.723	-0.617	-0.617
0.38654	0.7479	1222.63	3.023	3.211	3.239	3.243	-1.653	-0.872	-0.756	-0.756
0.44097	0.7501	1221.09	3.029	3.215	3.244	3.249	-1.759	-0.935	-0.812	-0.812
0.4835	0.7520	1219.77	3.034	3.218	3.249	3.254	-1.833	-0.973	-0.847	-0.847
0.58849	0.7574	1216.04	3.050	3.225	3.260	3.264	-1.921	-1.022	-0.879	-0.879
0.61515	0.7590	1214.91	3.055	3.229	3.263	3.267	-1.912	-1.023	-0.876	-0.876
0.69605	0.7644	1211.39	3.071	3.236	3.271	3.275	-1.896	-0.991	-0.830	-0.830
0.79594	0.7725	1206.25	3.097	3.250	3.282	3.285	-1.721	-0.870	-0.688	-0.688
0.90295	0.7839	1199.55	3.136	3.272	3.293	3.295	-1.303	-0.615	-0.406	-0.406
0.95321	0.7905	1195.93	3.160	3.287	3.299	3.299	-0.984	-0.448	-0.216	-0.216
At 318.15k										
0.08048	0.7317	1213.61	2.851	3.172	3.180	3.181	-0.899	-0.050	-0.164	-0.164
0.19017	0.7341	1212.25	2.858	3.175	3.193	3.195	-1.375	-0.240	-0.360	-0.360
0.28812	0.7369	1210.60	2.865	3.180	3.204	3.207	-1.508	-0.379	-0.505	-0.505
0.38654	0.7402	1208.52	2.875	3.186	3.215	3.219	-1.706	-0.486	-0.617	-0.617
0.44097	0.7424	1207.15	2.881	3.190	3.221	3.226	-1.800	-0.528	-0.662	-0.662
0.4835	0.7442	1205.95	2.887	3.194	3.227	3.231	-1.864	-0.552	-0.688	-0.688
0.58849	0.7495	1202.61	2.904	3.202	3.239	3.243	-1.940	-0.573	-0.712	-0.712
0.61515	0.7512	1201.54	2.909	3.206	3.242	3.246	-1.929	-0.569	-0.708	-0.708

0.69605	0.7565	1198.32	2.927	3.215	3.251	3.255	-1.916	-0.527	-0.668	-0.668
0.79594	0.7646	1193.51	2.955	3.230	3.263	3.266	-1.758	-0.410	-0.551	-0.551
0.90295	0.7760	1187.16	2.996	3.254	3.276	3.277	-1.369	-0.184	-0.323	-0.323
0.95321	0.7826	1183.71	3.021	3.270	3.282	3.282	-1.079	-0.043	-0.171	-0.171
2-Butanol+ Dodecane										
0.04602	0.7528	1312.74	3.273	3.232	3.233	3.234	-0.150	-0.020	0.000	-0.094
0.0507	0.7529	1312.32	3.271	3.232	3.233	3.234	-0.172	-0.028	0.000	-0.104
0.09287	0.7536	1309.26	3.257	3.230	3.232	3.234	-0.318	-0.105	-0.001	-0.185
0.18128	0.7555	1302.82	3.230	3.226	3.230	3.233	-0.567	-0.251	-0.001	-0.340
0.24985	0.7572	1297.76	3.211	3.222	3.228	3.232	-0.730	-0.348	-0.002	-0.443
0.30044	0.7586	1294.05	3.198	3.220	3.227	3.231	-0.835	-0.410	-0.002	-0.510
0.33974	0.7598	1291.23	3.189	3.218	3.226	3.231	-0.911	-0.451	-0.002	-0.555
0.38271	0.7612	1288.14	3.180	3.216	3.225	3.230	-0.979	-0.490	-0.002	-0.598
0.48939	0.7654	1280.62	3.163	3.211	3.222	3.228	-1.121	-0.552	-0.002	-0.670
0.59429	0.7707	1273.68	3.156	3.206	3.220	3.225	-1.199	-0.561	-0.002	-0.687
0.69831	0.7773	1267.06	3.160	3.203	3.218	3.222	-1.160	-0.507	-0.002	-0.640
0.80469	0.7860	1260.19	3.175	3.202	3.215	3.219	-0.966	-0.374	-0.001	-0.512
0.90245	0.7964	1253.5	3.203	3.204	3.213	3.215	-0.564	-0.167	-0.001	-0.307
0.95177	0.8028	1250.22	3.225	3.207	3.212	3.213	-0.253	-0.028	0.000	-0.166
At 298.15k										
0.04602	0.7455	1273.46	3.123	3.218	3.219	3.220	-0.366	-0.382	0.000	-0.077
0.0507	0.7455	1273.10	3.121	3.218	3.219	3.220	-0.390	-0.389	0.000	-0.085
0.09287	0.7462	1269.82	3.106	3.216	3.218	3.220	-0.540	-0.458	-0.001	-0.151
0.18128	0.7480	1263.38	3.079	3.211	3.216	3.219	-0.779	-0.589	-0.001	-0.277
0.24985	0.7496	1258.36	3.060	3.208	3.214	3.218	-0.929	-0.679	-0.001	-0.361
0.30044	0.7509	1254.67	3.046	3.206	3.213	3.218	-1.026	-0.736	-0.002	-0.414
0.33974	0.7522	1251.84	3.037	3.204	3.212	3.217	-1.095	-0.777	-0.002	-0.450
0.38271	0.7535	1248.76	3.028	3.202	3.211	3.217	-1.160	-0.816	-0.002	-0.484
0.48939	0.7576	1241.13	3.009	3.197	3.209	3.215	-1.286	-0.886	-0.002	-0.541

0.59429	0.7627	1234.11	3.000	3.193	3.207	3.212	-1.363	-0.916	-0.002	-0.552
0.69831	0.7692	1227.66	3.003	3.190	3.205	3.209	-1.346	-0.899	-0.002	-0.512
0.80469	0.7778	1221.36	3.020	3.189	3.203	3.206	-1.208	-0.827	-0.001	-0.407
0.90245	0.7882	1215.73	3.052	3.192	3.201	3.203	-0.880	-0.702	-0.001	-0.243
0.95177	0.7947	1213.24	3.079	3.195	3.200	3.201	-0.615	-0.616	0.000	-0.131
At 308.15k										
0.04602	0.7381	1234.92	2.973	3.197	3.198	3.199	-0.541	-0.148	0.000	-0.063
0.0507	0.7381	1234.48	2.970	3.197	3.198	3.199	-0.562	-0.153	0.000	-0.069
0.09287	0.7387	1231.07	2.954	3.195	3.197	3.198	-0.718	-0.204	-0.001	-0.123
0.18128	0.7404	1224.51	2.925	3.190	3.194	3.198	-0.951	-0.301	-0.001	-0.225
0.24985	0.7419	1219.48	2.906	3.187	3.193	3.197	-1.094	-0.365	-0.001	-0.293
0.30044	0.7432	1215.85	2.892	3.184	3.191	3.196	-1.184	-0.406	-0.002	-0.336
0.33974	0.7444	1213.01	2.883	3.182	3.190	3.195	-1.249	-0.434	-0.002	-0.365
0.38271	0.7457	1209.91	2.873	3.180	3.189	3.195	-1.308	-0.459	-0.002	-0.392
0.48939	0.7496	1202.2	2.852	3.175	3.187	3.192	-1.423	-0.501	-0.002	-0.436
0.59429	0.7546	1195.02	2.841	3.171	3.184	3.190	-1.495	-0.509	-0.002	-0.444
0.69831	0.7609	1188.52	2.842	3.168	3.182	3.187	-1.494	-0.479	-0.002	-0.409
0.80469	0.7694	1182.58	2.859	3.167	3.180	3.183	-1.397	-0.407	-0.001	-0.324
0.90245	0.7797	1177.79	2.894	3.169	3.178	3.180	-1.137	-0.296	-0.001	-0.192
0.95177	0.7863	1175.92	2.923	3.171	3.177	3.178	-0.914	-0.224	0.000	-0.103
At 318.15k										
0.04602	0.7306	1197.08	2.822	3.169	3.169	3.170	-0.673	0.065	0.000	-0.051
0.0507	0.7306	1196.62	2.819	3.168	3.169	3.170	-0.694	0.061	0.000	-0.056
0.09287	0.7312	1193.03	2.801	3.166	3.168	3.170	-0.852	0.025	-0.001	-0.100
0.18128	0.7326	1186.25	2.771	3.161	3.165	3.168	-1.084	-0.044	-0.001	-0.183
0.24985	0.7341	1181.2	2.750	3.158	3.163	3.167	-1.222	-0.088	-0.001	-0.238
0.30044	0.7353	1177.53	2.737	3.155	3.161	3.166	-1.307	-0.114	-0.001	-0.272
0.33974	0.7364	1174.71	2.727	3.153	3.160	3.165	-1.368	-0.132	-0.002	-0.296
0.38271	0.7377	1171.59	2.717	3.151	3.158	3.164	-1.421	-0.147	-0.002	-0.317

0.48939	0.7415	1163.8	2.695	3.145	3.155	3.161	-1.532	-0.166	-0.002	-0.352
0.59429	0.7462	1156.43	2.681	3.140	3.152	3.157	-1.601	-0.157	-0.002	-0.357
0.69831	0.7523	1149.84	2.679	3.136	3.149	3.153	-1.613	-0.118	-0.001	-0.328
0.80469	0.7606	1143.97	2.694	3.134	3.146	3.149	-1.542	-0.045	-0.001	-0.258
0.90245	0.7709	1139.65	2.729	3.135	3.143	3.145	-1.335	0.052	-0.001	-0.153
0.95177	0.7774	1138.24	2.759	3.137	3.142	3.143	-1.155	0.113	0.000	-0.082

Conclusion

From above discussion, it can be concluded that internal pressure, pseudo-grüneisen parameter and their excess values derived from isothermal compressibility, thermal expansion coefficient, density, heat capacity and ultrasonic speed at different temperatures and entire range of mole fraction and compared with theoretical data obtained from associated and non-associated model successfully. Non-associated model deals fair agreement with measured values because model was proposed for γ -meric non-electrolytic spherical type chain molecules. Positive values of excess pseudo-grüneisen parameter confirm the weak molecular interaction due to the electronic repulsion between non bonded electrons of binary components and favour the packing of unlike molecules where as negative values show strong molecular interaction between the binary components and predict the interstitial accommodation of liquid components.

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