Excess Internal Pressure and Excess Gruneisen Parameter of binary liquid mixtures at 308.15K

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Abstract : Internal pressure, Heat of vaporization, Excess internal pressure, and excess Gruneisen parameter have been computed for four binary liquid mixtures Methyl propanoate + n-heptane (x_2), Methyl propanoate + benzene (x_2), Methyl propanoate + chlorobenzene (x_2) and Methyl propanoate + 1,1,2,2 tetrachloroethane (x_2) from experimental data on speed of sound, viscosity, isothermal compressibility and isobaric coefficient by using empirical formulas. The observed values of the excess parameters plotted against the mole fraction of propanoate (x_1) have been explained on the basis of intermolecular-interaction suggesting strong interaction in Methyl propanoate + chlorobenzene (x_2) and Methyl propanoate + 1,1,2,2 tetrachloroethane (x_2). The values of excess functions provide an in-depth understanding of the inter-molecular interactions between the components.

Keywords : Internal pressure, Gruneisen Parameter, Excess functions, molecular interactions

Introduction

The internal pressure is the resultant of forces of attraction and repulsion between the constituents in the liquid system provides the estimate of pressure directed inward by cohesion. Internal pressure is found to be a very important parameter for explaining the various characteristics of liquid mixtures and to study the various chemical reactions initiated by ultrasonic waves[1]. Extensive work carried out on excess internal pressure[2-5] and still in progress. The Gruneisen parameter, a dimensionless constant generated by the molecular order and structure. In the quasi- crystalline model of lattice dynamics, the variation of anharmonicity in the lattice vibration frequency w_1 with molar volume V, can be given by microscopic Gruneisen Parameter [6-7]. The values of excess functions provide an in-depth understanding of the intermolecular interactions[8-10] between the components. In this present investigation attempt has been made to evaluate excess internal pressure, heat of vaporization and excess Gruneisen parameter in four binary liquid mixtures at 298.15K and the study has been extended to correlate this excess property with intermolecular interactions between the liquids.

Theoretical

The internal pressure *P*int in liquids can be also indirect evaluated from direct or indirect measurements of the isothermal compressibility βT and isobaric coefficient of thermal expansion α by using the well-known relation:

$$P_{\text{int}} = \left(\frac{\alpha T}{\beta_T} \right) \text{.....} \quad (1)$$

Empirical formula[11] for α and β_T in terms of velocity, density and temperature are as follows:

$$\alpha = \left(\frac{75.6x10^{-3}}{T^{\frac{1}{9}}.u^{\frac{1}{2}}.\rho^{\frac{1}{3}}} \right).\deg^{-1} \quad \text{and} \quad \beta_T = \left(\frac{1.71x10^{-4}}{T^{\frac{4}{9}}.u^{2}.\rho^{\frac{4}{3}}} \right).cm^{2}dyne^{-1}$$

From the above equations we have equation. 1

$$P_{\text{int}} = \left(44.2xT^{\frac{4}{3}}.u^{\frac{3}{2}}.\rho \right) \text{.....} \quad (2)$$

Above given both equations are very useful in direct computing the value of internal pressure from the experimental values of velocity and density, for binary liquid mixtures.

The excess internal pressure is defined as the difference between the internal pressure of the mixture ($P_{in(mix)}$) and that of an ideal mixture of the same composition given by the relation,

$$P_{in}^{E} = P_{in(mix)} - \{x_1.P_{in(1)} + x_2.P_{in(2)}\} \quad \ldots\ldots(3)$$

Here x_1, x_2 denotes the mole fraction of component 1 and 2 respectively.

The energy of vaporization ΔUvap may be obtained from the relation,

$$\Delta U_{vap} = (P_{\text{int}}.V_m) \quad \ldots\ldots(4)$$

Where Vm is the molar volume, is given by

$$V_m = \left(M_{eff} / \rho_m\right) \quad \ldots\ldots(5)$$

The Gruneisen parameter is a dimensionless measure of the change in entropy with volume or the thermal pressure and investigated through the relations:

$$\Gamma = \left(\frac{\alpha V}{\beta_T.Cv}\right) = \left(\frac{\alpha V}{\beta_S.Cp}\right) = \frac{V}{Cv}\left(\frac{\partial P}{\partial T}\right)_V \quad \ldots\ldots(6)$$

With the help of some thermodynamic relations, the expression for can be written as:

$$\Gamma = \left(\frac{C^2\alpha}{Cp}\right) = \left(\frac{\gamma - 1}{\alpha T}\right) \quad \ldots\ldots(7)$$

Adiabatic compressibility has been calculated from speed of sound (u) and density (ρ) of the medium using this relation :

$$\beta_S = \left(\frac{1}{u^2.\rho}\right) \quad \ldots\ldots(8)$$

The excess Gruneisen parameter is calculated using the relation:

$$\Gamma^{E} = \Gamma_{(mix)} - \{x_1.\Gamma_{(1)} + x_2.\Gamma_{(2)}\} \quad \ldots\ldots(9)$$

Table 1: viscosity, ultrasonic velocity, and thermal expansion coefficient for pure components a 308.15 K

Liquids	Viscosity mPas	Ultrasonic velocity ms^{-1}	Isothermal expansion coeff. kK^{-1}	Gruneisen parameter Γ
n-heptane	0.353	1095	1.23	3.3013
benzene	0.537	1255	1.22	3.9015
chlorobenzene	0.675	1224	1.06	4.0638
1,1,2,2 tetrachloroethane	0.406	1124	0.66	3.4333
methyl propanoate	0.437	1130	0.77	3.4496

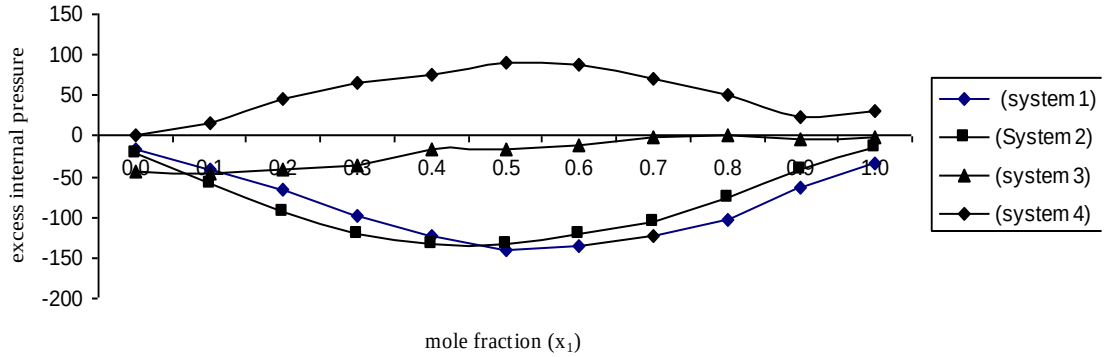
Table 2. Mole fraction x_1, density, internal pressure and excess internal pressure, excess Gruneisen parameter and heat of vaporization for binary liquid mixtures at 308.15K

Methyl propanoate + n-heptane					
x_1	ρ	Pint	$Pint^E$	Γ^E	ΔU_{vap}
	gm/cc	atm	atm		$KJmol^{-1}$
0.0447	0.572	1871.39	-37.64	0.2185	26.7
0.1083	0.5838	1896.96	-89.69	0.2263	26.6
0.1932	0.6006	1938.21	-152.07	0.2374	26.5
0.3018	0.6243	2000.66	-222.16	0.2526	26.5
0.4146	0.6503	2081.14	-279.36	0.2697	26.6
0.5227	0.6774	2173.98	-318.46	0.2871	26.8
0.5693	0.6938	2223.25	-326.07	0.2955	26.8
0.7002	0.7386	2390.14	-318.94	0.3206	27.2
0.7986	0.7788	2554.97	-274.21	0.3414	27.7
0.9016	0.8295	2781.47	-173.42	0.3652	28.5
0.9509	0.8587	2914.63	-100.43	0.3769	28.9
Methyl propanoate + benzene					
x_1	ρ	Pint	$Pint^E$	Γ^E	ΔU_{vap}
	gm/cc	atm	atm		$KJmol^{-1}$
0.0415	0.8609	3458.74	-7.98	-0.0990	30.5
0.1037	0.8558	3417.43	-23.87	-0.0676	30.6
0.2041	0.8522	3353.87	-46.40	-0.0174	30.5
0.3026	0.8497	3307.60	-52.41	0.0331	30.6
0.4053	0.8508	3263.53	-54.51	0.0856	30.5
0.4569	0.8526	3242.04	-54.91	0.1118	30.4
0.6013	0.8576	3184.35	-53.59	0.1853	30.2
0.7026	0.8639	3151.21	-45.32	0.2371	30.0
0.8018	0.8723	3125.00	-30.99	0.2880	29.9
0.9039	0.8816	3067.32	-16.94	0.3401	29.6
0.9674	0.8883	3084.01	-4.29	0.3727	29.5
Methyl propanoate + chlorobenzene					
x_1	ρ	Pint	$Pint^E$	Γ^E	ΔU_{vap}
	gm/cc	atm	atm		$KJmol^{-1}$
0.0485	0.527	3843.35	18.72	-0.0833	66.3
0.0993	0.5838	3812.31	27.17	-0.0562	63.9
0.2038	0.6006	3741.05	38.78	-0.0021	60.1
0.2614	0.6243	3696.95	40.06	0.0270	56.6
0.4087	0.6503	3576.22	35.37	0.1002	51.5
0.4556	0.6774	3536.43	32.54	0.1234	48.5
0.6041	0.6938	3418.32	31.43	0.1974	44.8
0.7011	0.7386	3341.72	31.25	0.2453	40.5
0.8064	0.7788	3255.77	28.26	0.2968	36.8
0.9054	0.8295	3168.95	19.44	0.3449	33.1
0.9486	0.8587	3125.86	10.38	0.3652	31.3
Methyl propanoate + 1,1,2,2tetrachloro ethane					
x_1	ρ	Pint	$Pint^E$	Γ^E	ΔU_{vap}
	gm/cc	atm	atm		$KJmol^{-1}$
0.0501	1.5415	5330.57	67.63	-0.0484	56.2
0.1021	1.5118	5255.51	112.35	-0.0149	55.9
0.2031	1.4493	5024.95	114.43	0.0467	56.1
0.3020	1.3829	4756.72	74.00	0.1039	53.3

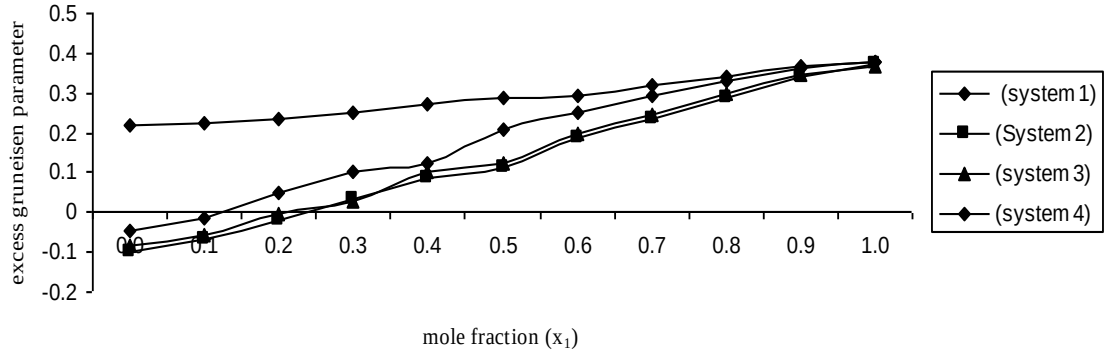
0.3398	1.3596	4658.10	62.44	0.1236	48.7
0.5038	1.2505	4238.55	20.64	0.2065	50.8
0.6012	1.1833	4000.04	6.48	0.2514	44.3
0.6946	1.1158	3776.97	-1.46	0.2914	41.6
0.7988	1.0402	3530.38	-8.04	0.3304	39.5
0.9016	0.9638	3301.87	0.24	0.3642	36.9
0.9481	0.9368	3200.92	6.39	0.3758	32.7

For binary liquid mixtures the values of internal pressure, Heat of vaporization evaluated by empirical equations (2) and (4) values of excess internal pressure and excess gruneisen parameter reported in Table 2. The required data for computation is taken from literature[12].

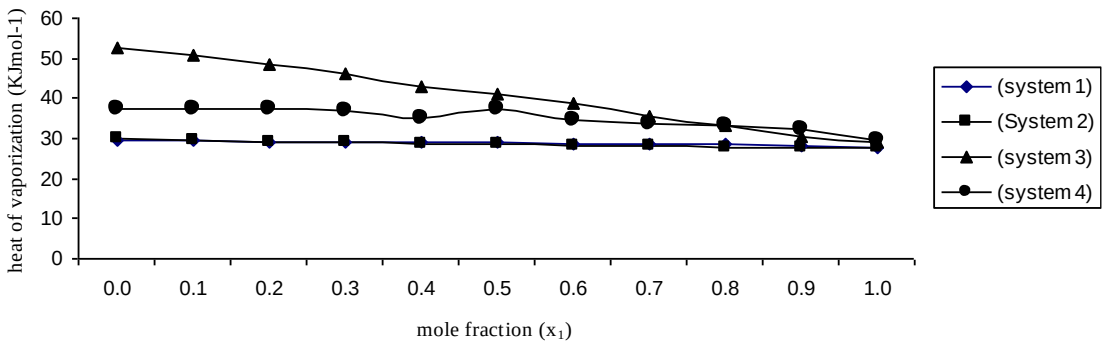
Graph 1: Mole fraction x_1, versus excess internal pressure for binary liquid mixtures at 308.15



Graph 2: Mole fraction x_1, versus excess internal pressure, excess pseudo gruneisen parameter for binary liquid mixtures at 308.15 K



Graph 3: Mole fraction x_1 versus Heat of Vaporization for binary liquid mixtures at 308.15 K



Result and Discussion:

A vigilant examination of table 2 shows that the excess internal pressure increases gradually, reach a maximum and decreases again. The values of heat of vaporization computed by equation () follow decreasing trend with decreasing the concentration of n-heptane , identical trend is reflected in rest three binary liquid mixtures; Methyl propanoate + benzene (x_2), Methyl propanoate + chlorobenzene (x_2) and Methyl propanoate + 1,1,2,2 tetrachloroethane (x_2). The values of heat of vaporization for the aforementioned binary system ; methyl propanoate + n-heptane is less than rest three binary liquid mixtures. This may be due to the fact that, the molecules with higher velocities are responsible for vaporization of a liquid and the boiling point of n-heptane is less than benzene, chlorobenzene and 1,1,2,2 tetrachloroethane.

For system; methyl-propanoate + benzene the values of excess internal pressure increase first and again decrease with increasing mole fraction of benzene. These changes can be explained by considering the n-π electron type specific interactions between the lone pairs of electrons on carbonyl group of esters and π-electrons of aromatic ring.

For system methyl-propanoate + chlorobenzene the values of excess internal pressure increase gradually and after maxima the values decreases, the O-Cl type specific interactions between the ester and chlorobenzene are responsible for this trend.

For system; methyl-propanoate + 1,1,2,2 tetrachloroethane values of excess internal pressure decreases with decreasing concentration of 1,1,2,2 tetrachloroethane. They can be considered due to the domination of interaction between the lone electron pairs of ester and Cl.

The negative values of Excess Pseudo Gruneisen parameter in these four binary systems indicate strong interactions between two liquids.

The values of heat of vaporization follow a decreasing trend with decreasing concentration of x_2 The values of heat of vaporization for binary system; Methyl propanoate + heptane (x_2) is less than rest of the binary systems; Methyl propanoate + benzene (x_2), Methyl propanoate + chlorobenzene (x_2) and Methyl propanoate + 1,1,2,2 tetrachloroethane (x_2). This may be due to the fact that, the molecules with higher velocities are responsible for vaporization of a liquid and the boiling point of n-heptane (x_2) is less than benzene (x_2), chlorobenzene (x_2) and 1,1,2,2 tetrachloroethane (x_2).

Conclusion:

As chlorobenzene (x_2) and 1,1,2,2 tetrachloroethane (x_2) are more polarizable than n-heptane (x2) and benzene (x2), So greater interaction is observed in binary systems containing chlorobenzene (x_2) and 1,1,2,2 tetrachloroethane (x_2).

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