Indian Journal of Chemical Technology
Vol. 23, November 2016, pp.469-477

Internal pressure, excess internal pressure and pseudo-Gruneisen parameter of binary systems from associated and non-associated models

R K Shukla*[,1], Kirti Tenguriya[2], Sadhna Shukla[3], Manish Tiwari[3] & Sonu Dwivedi[4]
[1]Department of Chemistry, V.S.S.D. College, Kanpur 208 002, India.
[2]Department of Chemistry, Govt. Science College, Gwalior, India
[3]Department of Chemistry, M G C G University, Chitrakoot, Satna, India
[4]Department of Chemistry, DBS College, Dehradun, Uttarakhand, India
E-mail: rajeevshukla47@rediffmail.com

Received 12 August 2014; accepted 26 February 2015

Density and speed of sound have been measured earlier for binary liquid mixtures formed by formamide, N-methylacetamide, di-methylformamide and di-methylacetamide with acetonitrile at 293.15, 298.15, 303.15, 308.15 and 313.15 K and atmospheric pressure over the whole concentration range. Pseudo-Gruneisen parameter and internal pressure have been derived from the measured values of density and ultrasonic velocity. These values are compared with the theoretical values obtained by the utilization of Flory theory, Ramaswamy and Anbananthan model and model suggested by Glinski to predict the behaviour of weakly interacting liquids. The observed properties derived from measured data are fitted to Redlich-Kister polynomial relation to estimate the binary coefficients and standard errors. Excess internal pressure parameter for these binary mixtures is also computed to study the molecular interactions involved in the liquid systems.

Keywords: Pseudo-Gruneisen parameter, Internal pressure, Flory theory, Ramaswamy and Anbananthan model, Redlich-Kister

The role of internal pressure in liquid solution thermodynamics was recognized by Hildebrand[1]. The use of this property for a long time was qualitative but recently its usefulness has been explored for quantitative study of intermolecular forces. Pioneer attempts have been made by several workers[2-8] to study the significance and its correlation with other properties. A liquid under a small isothermal volume expansion does work against the cohesive force which causes the change in the internal energy (E). The function $(\partial E/\partial V)_T$ is called internal pressure. Hildebrand[1-2] showed that for non-polar liquids, $(\partial E/\partial V)_T = n\ \Delta E_{vap}/V$, where ΔE_{vap} represents the energy of vaporization of the liquid and V its molar volume. The quantity n approaches energy density. For polar liquids n ranges from 0.32-1.624. Internal pressure and cohesive energy density (c.e.d.), evidently, do not reflect the same physical property of these liquids. Our one of the aim is to analyze the physical significance of internal pressure and cohesive energy density and to demonstrate the usefulness of both properties.

Two liquids do not completely mix if one liquid has much greater cohesion than the other. Conversely, molecules in liquids of similar cohesion are just as likely to interact and mix with each other as with their own kind. Any interaction between unlike molecules enhances the change of miscibility. Hildebrand[1] has referred to the square root of c.e.d. as the solubility parameter because of its frequent use in solubility problems. The internal pressure of liquid mixtures were computed from the knowledge of thermal expansion coefficient (α) and isothermal compressibility (β_T).

The internal pressure can be computed by indirect methods as suggested by Suryanarayan[9]. In recent past, substantial amount of work has been carried out by many workers to study the excess thermodynamic functions like excess internal pressure; excess energy of vaporization, excess pseudo-Gruneisen parameter and is still in progress[9-13].

Gruneisen parameter is an important tool to study the thermodynamic and other properties of solid crystalline lattice[14]. The concept of anharmonicity of the lattice is characterized by the Gruneisen parameter. It is well established that liquids support a quasi-crystalline model for their structure, the lattice nature being increased at high pressure and low temperature and the Gruneisen parameter can also be used to study them. Its pseudo counterpart has been found to be suitable to investigate the internal structures, clustering phenomenon and other quasi crystalline properties of liquids including liquid mixtures[15-18], liquefied gases[19], liquid metal alloys[20] and higher alkanes[15].

In the present investigation, internal pressure, excess internal pressure and Pseudo-Gruneisen parameter were derived from the measured values of density and ultrasonic velocity[21] for binary liquid mixtures formed by formamide, N-methylacetamide (NMA), di-methylformamide (DMF) and di-methylacetamide (DMA) with acetonitrile at 293.15, 298.15, 303.15, 308.15 and 313.15 K and atmospheric pressure over the whole concentration range. A comparison of experimental and theoretical speed of sound is provided in Table 1. These derived values of internal pressure were compared with the theoretical values obtained by the utilization of Flory theory[22,23], Ramaswamy and Anbananthan model[24] and model suggested by Glinski[25] to predict the behavior of weakly interacting liquids. The observed properties derived from measured data were fitted to Redlich-Kister polynomial relation[26] to estimate the binary coefficients and standard errors.

Computational methods

Flory theory

Assuming two body interactions, Flory evaluated the reduced and characteristic parameters of the liquid mixture from the reduced equation of state derived from the resulting partition function as;

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

where, $\tilde{P} = \frac{P}{P^*}$,$\tilde{T} = \frac{T}{T^*}$, and $\tilde{V} = \frac{V}{V^*}$

where $\tilde{P}\ \tilde{T}\ \tilde{V}$ are reduced parameters and $P^*, T^*, V^*$are characteristic parameters. The coefficient of thermal expansion, α, is evaluated from the reduced equation of state as;

Table 1 — Comparison of density and sound velocity with literature data for pure components at 293.15, 298.15, 303.15, 308.15 and 313.15 K

Compound	$\alpha \times 10^3$ K	$\beta_T \times 10^{12}$ Pa	V/cm^{3}mole^{-1}	T	ρ_{exp}/g.cm^{-3}	ρ^*_{lit}/g.cm^{-3}	u_{exp}/ms^{-1}	U^*_{lit}/ms-^{1}
Acetonitrile	1.2762	108.84	51.53	293.15	0.7965	0.7822	1305.5	1347.1
	1.2943	113.54	52.55	298.15	0.7811	0.77649	1290.1	1326.3
	1.3151	119.10	53.08	303.15	0.7733	0.77125	1263.4	1293.4
	1.3300	123.18	53.55	308.15	0.7665	-	1245.1	1263.5
	1.3420	126.54	53.97	313.15	0.7605	-	1230.5	1242.7
Formamide	0.9431	43.92	39.78	293.15	1.1320	1.1339	1625.8	1647.9
	0.9515	45.11	39.89	298.15	1.1290	1.12915	1601.0	1626.3
	0.9570	45.89	40.03	303.15	1.1250	-	1585.2	1607.2
	0.9594	46.24	40.17	308.15	1.1210	1.12068	1577.2	1585.1
	0.9656	47.15	40.51	313.15	1.1117	-	1565.1	1571.3
NMA	1.1095	71.51	76.44	293.15	0.9563	-	1425.8	1455.2
	1.1224	74.03	76.85	298.15	0.9512	-	1401.0	1431.6
	1.1349	76.53	76.93	303.15	0.9502	0.9520	1373.8	1411.8
	1.1440	78.38	77.20	308.15	0.9468	0.9460	1355.8	1387.8
	1.1364	76.85	77.72	313.15	0.9405	-	1370.5	1375.2
DMF	1.0844	66.76	76.52	293.15	0.9551	0.94873	1476.8	1517.2
	1.0899	67.79	76.92	298.15	0.9501	0.94387	1465.2	1496.4
	1.0970	69.12	77.59	303.15	0.9419	0.9412	1454.1	1481.3
	1.1108	71.76	78.11	308.15	0.9357	-	1428.2	1463.2
	1.1187	73.31	78.38	313.15	0.9325	0.9310	1411.2	1432.2
DMA	1.0839	66.67	90.53	293.15	0.9623	0.9615	1470.5	1420.6
	1.0968	69.09	91.68	298.15	0.9502	0.97633	1451.3	1501.3
	1.1097	71.56	93.07	303.15	0.9360	0.93169	1435.1	1468.7
	1.1190	73.36	94.00	308.15	0.9268	-	1421.5	1438.3
	1.1255	74.64	94.47	313.15	0.9221	0.9232	1409.0	1422.6

* Ref.30

$$\alpha_{Flory} = \frac{1}{T\left[\dfrac{1}{3(\tilde{V}^{1/3}-1)-1}\right]} \qquad ...(2)$$

and adiabatic compressibility, β_s is given by,

$$\beta_s = \frac{1}{u^2\rho} \qquad ...(3)$$

where, u and ρ are speed of sound and density of binary liquid mixture. By combining above equations Pseudo-Greneisen parameter for liquid mixtures is obtained as;

$$\tau_{Flory} = \frac{1}{T}\left[\frac{1}{\beta_s} - \gamma_P - \frac{1}{\alpha}\right] \qquad ...\ (4)$$

where γ_P is the thermal pressure coefficient and related to the following expression as;

$$\gamma_P = \frac{P^*}{T\tilde{V}^2} \qquad ...(5)$$

γ_P is also related to internal pressure of the liquid mixture as;

$$P_{i_{Flory}} = T.\gamma_P \qquad ...(6)$$

For observed value of Pesudo-Gruneisen parameter, γ_P is evaluated by the relation as;

$$\gamma_P = \frac{\alpha}{\beta_T} \qquad ...(7)$$

Thermal expantion coefficient, α and adiabatic compressibility, β_T are defined as;

$$\alpha = (0.0191 \times \beta_T)^{1/4} \qquad ...(8)$$

$$\beta_T = 1.71 \times 10^{-3} / T^{4/9} \times u^2 \times \rho^{4/3} \qquad ...(9)$$

Ramswamy and Anbananthan Model

Ramswamy and Anbananthan[24] proposed the model based on the assumption of linearity of acoustic impedance with the mole fraction of components. Further it is assumed, that an equilibrium physical property such as viscosity, refractive index, surface tension etc which are based on linearity can also be predicted. Glinski[25] assumed that when solute is added to solvent the molecules interact according to the equilibrium,

$$A+B \leftrightarrow AB \qquad ...(10)$$

and the association constant, K_{as}, can be defined as;

$$K_{as} = \frac{[AB]}{[A][B]} \qquad ...(11)$$

where $[A]$ is amount of solvent and $[B]$ is amount of solute in the liquid mixture. By applying the condition of linearity with composition, internal pressure can be obtained as;

$$Pi_{cal} = x_A Pi_A + x_{AB} Pi_{AB} \qquad ...(12)$$

where x_A, $x_{AB,}Pi_A$ and Pi_{AB} and Pi_{cal} are the mole fraction of A, mole fraction of associate AB, internal pressure of A, internal pressure of associate AB and calculated internal pressure respectively. The associate AB cannot be obtained in its pure form. Following simplifications have been made in Eq. (12), firstly, molar concentration term should be replaced by activities for concentrated solution and second, the equilibrium reaction is not complete by definition; i.e. there are also molecules of non-associated component present in the liquid mixture even prevailing in the high solute content. The Eq (12) takes the form,

$$Pi_{cal} = [x_A Pi_A + x_B Pi_B + x_{AB} Pi_{AB}] \qquad ...(13)$$

The general idea of this model can be, however, exploited as;

$$K_{as} = \frac{[AB]}{(C_A - [AB])(C_B - [AB])} \qquad ...(14)$$

where C_A and C_B are initial molar concentrations of the components. One can take any value of association constant, K_{as}, and calculate the equilibrium value of [AB] for every composition of the mixture. Replacing molar concentration by equi-molar activities for concentrated solution, Eq. (14) becomes,

$$K_{as} = \frac{a_{AB}}{(a_A - a_{AB})(a_B - a_{AB})} \qquad ...(15)$$

where a_A, a_B and a_{AB} are the activity of component A, Component B and associate, AB respectively.

Similarly, assuming any value of internal pressure for hypothetical pure component AB, the internal pressure of liquid mixture, Pi_{cal} can be calculated by substituting the value of association constant. Now, it is possible to compare the internal pressure calculated using Eq (14) with the experimental values. On changing both the adjustable parameters K_{as} and P_{iAB} gradually, one can get different values of the sum of squares of deviations,

$$S = \Sigma (Pi_{obs} - Pi_{cal})^2 \qquad ...(16)$$

where Pi_{obs} and Pi_{cal} are the observed and calculated internal pressure respectively.

The minimum value of *S* can be obtained theoretically by a pair of the fitted parameters. But we found that for some K_{as} and Pi_{AB}, the value of *S i*s high and changes rapidly, and for others, it is low and changes slowly when changing the fitted parameters. The condition which is prevailing in the process of adjustment is that the value of Pi_{AB} should not be much lower than the lowest Pi_{obs} of the system or much higher than the highest one. Quantitatively, it should be reasonable to accept the pair of adjustable parameters K_{as} and Pi_{AB} which has the physical sense and which reproduces the experimental physical property satisfactorily.

On inspecting the results obtained from Ramaswamy and Anbananthan model, Glisnki[25] suggested the equation assuming additivity with the volume fraction, ϕ of the components, the refined version of Natta and Baccaredda model[27] as,

$$Pi_{cal} = \frac{Pi_A Pi_B Pi_{AB}}{\phi_A Pi_B Pi_{AB} + \phi_B Pi_A Pi_{AB} + \phi_{AB} Pi_A Pi_B} \quad ...(17)$$

wherePi$_{cal}$ is the theoretical internal pressure of binary liquid mixture, ϕ_A, ϕ_B are the volume fractions of component A and B and Pi_A, Pi_B and Pi_{AB} are theinternal ofcomponents A, B and AB. The numerical procedure and determination of association constant, K_{as}, were similar to that described before and the advantage of this method as compared with the earlier one was that the data on densities of liquid mixture are not necessary except those of pure components needed to calculate the volume fractions

Results and Discussion

Relations between association phenomenons in liquids were analyzed earlier[28] by considering van der Waals equation of state which was based only on simple averaged geometrical deviations without analyzing the system in terms of equilibrium. The association phenomenon has been related usually the deviation of different quantities from additivity. Ramaswami and Anbananthan derived the model based on the assumption of linearity of acoustic impedance with the mole fraction of components which was corrected[25] and tested[28] to predict the associational behaviour. The quantities analyzed were refractive index, molar volume, viscosity, intermolecular free length. Prediction of internal pressure and pseudo-Gruneisen parameter from this approach is our first attempt. The results of fittings obtained from the model were utilized properly. The basic doubt regarding this model except the assumption of linearity of internal pressure and pseudo-Gruneisen parameter with mole fraction is that these liquids have poor affinity to form dimmers. The calculations were performed using a computer program which allows fittings easily both the adjustable parameters simultaneously or the parameters were changed manually.

We constructed the data sheet in a computer program with association constant K_{as} and $Pi_{A,B}$ as the fitted parameters. $Pi_{A,B}$ is the internal pressure in the pure component AB; i.e. a hypothetical liquid having only the associate AB. On changing these parameters, the equilibrium concentrations of species [A], [B] and [AB] will change and the internal pressure pseudo-Gruneisen parameter can be computed. The difference between observed and theoretical values for internal pressure and pseudo-Gruneisen parameter is used to obtain the sum of squares of deviation. It is assumed that in solution three associates instead of two are formed (A, B and AB). Thevalues of internal pressure and pseudo-Gruneisen parameter in pure associate can be treated as a fitted one with the value of K_{as}.

The standard deviation ΔPi can be represented mathematically by Redlich-Kister polynomial equation[26] for correlating the experimental data as;

$$y = x_i(1-x_1)\sum_{i=0}^{p} A_i(2x_1-1)^i \quad ...(18)$$

where y refers to deviation in internal pressure y (ΔPi), x_1 is the mole fraction and A_i is the coefficient. The values of coefficients were determined by a multiple regression analysis based on the least square method and are summarized along with the standard deviations between the experimental and fitted values of the respective function in Table 2. The standard deviation is defined by,

$$\delta = \left[\sum_{i=1}^{m} (y_{\exp} - y_{Cal})^2 \Big/ (m-p) \right]^{1/2} \quad ...(19)$$

where m is the number of experimental points and p is the number of adjustable parameters. The values of standard deviations lie between 0.0047 – 0.03723 TP a respectively.

The absolute average percent deviations (AAPD) in internal pressure, excess internal pressure and pseudo-Gruneisen parameter obtained from different models are provided in Table 3 whereas mixture data are presented in Table 4. A care full perusal of Tables 3 and 4 indicate

Table 2 — Coefficients of the redlich-kister equation and standard deviations (δ) for internal pressure of binary liquid mixtures at various temperatures.

Acetonitrile+Formamide	T	$A_0/_{\mathrm{TPa}}$	$A_1/_{\mathrm{TPa}}$	$A_2/_{\mathrm{TPa}}$	$A_3/_{\mathrm{TPa}}$	$\delta/_{\mathrm{TPa}}$
ΔPi	293.15	-0.40717	0.351245	-0.292010	-0.6776	0.00893
	298.15	-0.58225	0.142979	-0.065120	-0.8266	0.01073
	303.15	-0.18255	-0.055030	0.418638	0.3257	0.01162
	308.15	-0.55495	-0.151030	0.380918	5.7951	0.03723
	313.15	-0.21226	0.434801	0.863306	3.4910	0.03547
Acetonitrile+NMA						
ΔPi	293.15	-0.2378	-0.0435	-0.2048	-0.1847	0.0047
	298.15	-0.3369	0.1072	0.3379	-0.9842	0.0140
	303.15	-0.3188	0.1144	0.3243	-1.2755	0.0103
	308.15	-0.1376	-0.5202	-0.8697	1.4112	0.0278
	313.15	0.0694	-0.7276	-1.1805	2.1434	0.0227
Acetonitrile+DMF						
ΔPi	293.15	-0.2742	-0.4868	-0.3938	1.1237	0.0252
	298.15	-0.3732	-0.2664	0.0462	0.3930	0.0125
	303.15	-0.4591	-0.0241	-0.1198	-0.5562	0.0100
	308.15	-0.4651	-0.1541	-0.4590	0.1090	0.0138
	313.15	-0.4732	-0.5292	-0.3560	0.6609	0.0118
Acetonitrile+DMA						
ΔPi	293.15	-0.5459	0.0538	0.2031	-1.1486	0.0148
	298.15	-0.5004	-0.0729	0.1148	-0.4339	0.0104
	303.15	-0.3823	-0.1695	0.0627	-0.0565	0.0112
	308.15	-0.4337	-0.2263	-0.0142	0.2017	0.0060
	313.15	-0.3747	-0.3355	-0.0572	0.7105	0.0056

Table 3 — Comparison of absolute average percent deviation (AAPD) values obtained from various liquid state mode Acetonitrile+Formamide

T	K_{as}	τ_{Flory}	τ_{RS}	τ_{GLI}	$Pi_{\mathrm{Flory/TPa}}$	$Pi_{\mathrm{RS/TPa}}$	$Pi_{\mathrm{GLI/TPa}}$	$Pi^{E}_{\mathrm{Flory/TPa}}$	$Pi^{E}_{\mathrm{RS/TPa}}$	$Pi^{E}_{\mathrm{GLI/TPa}}$
293.15	0.0001	4.04	3.49	0.94	9.19	2.59	5.30	-0.21	0.13	0.13
298.15	0.0001	6.72	5.38	0.95	9.77	5.58	8.23	-0.13	0.11	0.09
303.15	0.0001	4.23	5.83	1.03	3.44	4.34	2.35	-0.13	0.09	0.09
308.15	0.0001	6.73	4.42	5.79	7.74	7.92	15.10	-0.63	-0.71	0.64
313.15	0.0001	6.72	5.96	5.09	5.55	3.63	14.64	0.54	0.60	0.46
Acetonitrile+NMA										
293.15	0.0001	5.12	4.65	0.23	1.69	2.15	1.49	0.14	0.09	0.11
298.15	0.0002	7.26	6.93	0.21	1.79	2.58	2.08	0.22	0.11	0.12
303.15	0.0002	8.15	7.65	0.20	1.46	3.39	2.80	0.23	0.09	0.11
308.15	0.0002	23.01	17.18	0.20	6.19	2.99	2.63	0.16	0.07	0.09
313.15	0.0002	6.17	6.45	0.23	7.88	1.96	1.92	0.33	0.05	0.08
Acetonitrile+DMF										
293.15	0.0001	4.88	3.95	0.29	3.14	3.36	2.50	0.12	0.09	0.07
298.15	0.0001	6.87	6.22	0.28	2.22	3.25	2.43	0.21	0.11	0.12
303.15	0.0001	8.51	7.47	0.29	3.51	5.02	4.18	0.22	0.17	0.12
308.15	0.0001	9.45	8.06	0.29	4.66	6.39	5.57	0.23	0.13	0.17
313.15	0.0001	10.06	8.82	0.28	5.05	6.29	5.50	0.24	0.15	0.15
Acetonitrile+DMA										
293.15	0.0001	6.35	4.86	0.46	5.71	5.33	4.03	0.16	0.17	0.13
298.15	0.0001	7.91	6.78	0.45	3.20	4.94	3.67	0.24	0.14	0.12
303.15	0.0001	7.98	7.19	0.48	2.49	4.08	2.71	0.25	0.09	0.08
308.15	0.0001	8.92	8.04	0.49	3.06	4.73	3.33	0.26	0.11	0.09
313.15	0.0001	8.97	8.35	0.50	2.72	4.08	2.65	0.27	0.09	0.09

Table 4 — Experimental densitiy (ρ), experimental ultrasonic velocity (u$_{Exp}$) , observed pseudo gruniesen parameter(τ$_{obs}$), observed internal pressure (Pi$_{obs}$), and theoretical values of pseudo gruniesen parameter and internal pressure obtained from various models for binary liquid mixtures at various temperatures.

Acetonitrile+Formamide

x$_1$	ρ$_{Exp}$/ g.cm^{-3}	u$_{Exp}$/ m.s^{-1}	Pi$_{obs}$ 10^{-9}Pa	Pi$_{Flory}$ 10^{-9}Pa	Pi$_{RS}$ 10^{-9}Pa	Pi$_{Gli}$10^{-9}Pa
293.15						
0.1225	1.1258	1605.8	6.402	5.833	6.288	6.171
0.2390	1.0992	1585.6	6.115	5.429	5.906	5.729
0.3499	1.0835	1575.9	5.949	5.073	5.600	5.398
0.4557	1.0405	1525.9	5.458	4.757	5.213	5.013
0.5567	1.0102	1469.8	5.011	4.476	4.897	4.715
0.6533	0.9705	1425.8	4.598	4.223	4.553	4.401
0.7456	0.9403	1386.9	4.275	3.997	4.275	4.158
0.8340	0.9015	1375.3	4.042	3.792	3.968	3.890
0.9187	0.8503	1355.9	3.737	3.606	3.636	3.598
298.15						
0.1225	1.1015	1590.6	6.144	5.815	5.984	5.872
0.2390	1.0825	1583.6	5.993	5.403	5.672	5.500
0.3499	1.0657	1576.9	5.899	5.042	5.430	5.232
0.4557	1.0345	1535.8	5.458	4.722	5.056	4.860
0.5567	0.9985	1490.5	5.067	4.438	4.751	4.573
0.6533	0.9624	1476.9	4.797	4.185	4.417	4.269
0.7456	0.9351	1409.2	4.378	3.957	4.193	4.077
0.8340	0.8792	1389.8	4.014	3.752	3.808	3.732
0.9187	0.8492	1345.9	3.695	3.567	3.570	3.532
303.15						
0.1225	1.0998	1525.9	5.903	5.831	6.018	5.895
0.2390	1.0735	1498.2	5.586	5.405	5.642	5.456
0.3499	1.0538	1456.8	5.256	5.032	5.341	5.129
0.4557	1.0258	1402.5	4.870	4.703	5.059	4.846
0.5567	0.9802	1367.5	4.461	4.411	4.651	4.462
0.6533	0.9594	1335.8	4.219	4.151	4.406	4.245
0.7456	0.9256	1290.5	3.881	3.918	4.131	4.007
0.8340	0.8728	1259.8	3.502	3.708	3.742	3.662
0.9187	0.8402	1220.2	3.223	3.519	3.502	3.461
308.15						
0.1225	1.0856	1555.8	6.154	5.884	5.940	4.638
0.2390	1.0568	1525.8	5.813	5.443	5.490	4.727
0.3499	1.0215	1490.5	5.400	5.058	5.047	4.747
0.4557	0.9856	1485.9	5.217	4.718	4.702	4.792
0.5567	0.9508	1475.9	4.956	4.418	4.350	4.768
0.6533	0.9256	1456.8	4.758	4.150	4.123	4.827
0.7456	0.8809	1399.8	4.240	3.911	3.792	4.711
0.8340	0.8405	1366.9	3.906	3.696	3.532	4.629
0.9187	0.8028	1260.8	3.295	3.502	3.293	4.530
313.15						
0.1225	1.0807	1543.8	6.158	5.900	6.041	5.303
0.2390	1.0559	1525.8	5.939	5.455	5.703	5.345
0.3499	1.0158	1490.5	5.518	5.066	5.283	5.268
0.4557	0.9758	1475.8	5.223	4.724	4.891	5.173
0.5567	0.9365	1425.6	4.756	4.421	4.524	5.062
0.6533	0.8905	1382.5	4.301	4.151	4.134	4.880
0.7456	0.8726	1364.8	4.123	3.910	3.902	4.851

Acetonitrile+NMA

x$_1$	ρ$_{Exp}$/ g.cm^{-3}	u$_{Exp/m.s}$$^{-1}$	Pi$_{obs}$ 10^{-9}Pa	Pi$_{Flory}$ 10^{-9}Pa	Pi$_{RS}$ 10^{-9}Pa	Pi$_{Gli}$10^{-9}Pa
293.15						
0.5757	0.8895	1386.7	4.046	3.967	3.915	3.955
0.6808	0.8764	1375.9	3.954	3.844	3.817	3.853
0.7614	0.8658	1359.1	3.838	3.747	3.733	3.763
0.8282	0.8465	1346.8	3.699	3.663	3.614	3.638
0.8821	0.8351	1335.8	3.611	3.594	3.545	3.563
0.9290	0.8252	1325.8	3.528	3.532	3.481	3.492
0.9685	0.8051	1315.5	3.403	3.480	3.379	3.384
298.15						
0.2733	0.9305	1389.2	4.240	4.257	4.155	4.183
0.4481	0.9197	1382.4	4.163	4.073	4.024	4.060
0.5757	0.8807	1375.1	3.951	3.930	3.788	3.824
0.6808	0.8704	1369.4	3.882	3.807	3.696	3.728
0.7614	0.8595	1346.8	3.742	3.709	3.617	3.644
0.8282	0.8405	1325.8	3.570	3.625	3.503	3.524
0.8821	0.8305	1300.4	3.427	3.555	3.438	3.453
0.9290	0.8205	1320.8	3.466	3.494	3.376	3.386
0.9685	0.8015	1300.9	3.305	3.441	3.277	3.281
303.15						
0.2733	0.9108	1372.6	4.166	4.224	4.034	4.061
0.4481	0.8998	1375.2	4.132	4.035	3.904	3.939
0.5757	0.8712	1355.8	3.910	3.889	3.714	3.748
0.6808	0.8652	1335.8	3.824	3.763	3.665	3.696
0.7614	0.8501	1301.5	3.593	3.662	3.544	3.570
0.8282	0.8357	1301.0	3.548	3.577	3.472	3.493
0.8821	0.8256	1298.5	3.496	3.506	3.407	3.422
0.9290	0.7958	1315.8	3.437	3.444	3.264	3.273
0.9685	0.7853	1280.5	3.259	3.390	3.207	3.211
308.15						
0.2733	0.9007	1355.7	4.133	10.039	3.996	4.022
0.4481	0.8795	1366.3	4.089	8.420	3.822	3.855
0.5757	0.8654	1285.3	3.688	7.229	3.717	3.751
0.6808	0.8556	1301.0	3.713	6.221	3.625	3.656
0.7614	0.8456	1295.8	3.648	5.469	3.546	3.571
0.8282	0.8298	1291.5	3.544	4.845	3.432	3.452
0.8821	0.8198	1275.5	3.437	4.359	3.367	3.381
0.9290	0.7902	1290.5	3.370	3.938	3.224	3.233
0.9685	0.7805	1235.8	3.118	3.594	3.166	3.170
313.15						
0.2733	0.8798	1345.9	4.084	4.529	4.022	4.053
0.4481	0.8697	1285.9	3.771	4.266	3.867	3.907
0.5757	0.8556	1275.6	3.683	4.062	3.745	3.784
0.6808	0.8425	1293.5	3.673	3.888	3.595	3.630
0.7614	0.8346	1275.6	3.554	3.750	3.506	3.535
0.8282	0.8194	1245.8	3.389	3.633	3.425	3.448
0.8821	0.8008	1265.1	3.384	3.537	3.311	3.328
0.9290	0.7824	1275.6	3.340	3.452	3.203	3.214
0.9685	0.7615	1225.9	3.066	3.379	3.100	3.105

(*Contd.*)

Table 4 — Experimental densitiy (ρ), experimental ultrasonic velocity (u_{Exp}) , observed pseudo gruniesen parameter(τ_{obs}), observed internal pressure (Pi_{obs}), and theoretical values of pseudo gruniesen parameter and internal pressure obtained from various models for binary liquid mixtures at various temperatures. (*Contd.*)

x_1	ρ_{Exp}/ g.cm^{-3}	u_{Exp}/ m.s^{-1}	Pi_{obs} 10^{-9}Pa	Pi_{Flory} 10^{-9}Pa	Pi_{RS} 10^{-9}Pa	Pi_{Gli}10^{-9}Pa
0.8340	0.8405	1300.8	3.704	3.693	3.641	4.757
0.9187	0.7992	1260.8	3.367	3.497	3.354	4.595
		Acetonitrile+DMF				
293.15						
0.2142	0.9391	1470.2	4.666	4.522	4.523	4.557
0.3802	0.9297	1438.0	4.466	4.322	4.343	4.392
0.5126	0.9158	1426.9	4.366	4.151	4.193	4.246
0.6206	0.8957	1390.8	4.110	4.005	4.020	4.070
0.7104	0.8748	1386.7	3.955	3.879	3.821	3.864
0.7863	0.8569	1385.7	3.906	3.768	3.723	3.758
0.8513	0.8354	1375.6	3.773	3.670	3.591	3.618
0.9075	0.8253	1356.7	3.652	3.584	3.510	3.527
0.9567	0.7902	1325.8	3.358	3.506	3.309	3.317
298.15						
0.2142	0.9342	1456.2	4.550	4.539	4.417	4.450
0.3802	0.9272	1436.1	4.456	4.326	4.283	4.330
0.5126	0.9215	1415.8	4.315	4.146	4.132	4.182
0.6206	0.8901	1389.9	4.060	3.993	3.915	3.962
0.7104	0.8721	1379.2	3.923	3.860	3.761	3.801
0.7863	0.8504	1365.4	3.776	3.744	3.620	3.653
0.8513	0.8344	1348.7	3.620	3.641	3.489	3.514
0.9075	0.8248	1325.8	3.485	3.551	3.409	3.425
0.9567	0.7899	1301.9	3.267	3.471	3.251	3.259
303.15						
0.2142	0.9304	1452.8	4.636	4.543	4.448	4.482
0.3802	0.9255	1431.8	4.536	4.319	4.299	4.348
0.5126	0.9192	1414.8	4.407	4.130	4.137	4.189
0.6206	0.8892	1381.0	4.112	3.969	3.911	3.960
0.7104	0.8706	1371.8	3.979	3.829	3.750	3.792
0.7863	0.8584	1360.8	3.886	3.708	3.646	3.681
0.8513	0.8261	1340.5	3.667	3.601	3.469	3.494
0.9075	0.8259	1320.0	3.583	3.506	3.426	3.443
0.9567	0.7853	1299.1	3.330	3.422	3.225	3.233
308.15						
0.2142	0.9280	1450.2	4.725	4.505	4.429	4.463
0.3802	0.9234	1425.1	4.554	4.284	4.239	4.286
0.5126	0.9065	1401.0	4.391	4.098	4.081	4.132
0.6206	0.8801	1371.1	4.111	3.939	3.859	3.906
0.7104	0.8647	1369.2	4.009	3.801	3.701	3.741
0.7863	0.8561	1352.1	3.934	3.681	3.641	3.675
0.8513	0.8248	1335.8	3.683	3.576	3.424	3.448
0.9075	0.8234	1311.0	3.581	3.483	3.382	3.399
0.9567	0.7805	1282.1	3.294	3.401	3.183	3.191
313.15						
0.2142	0.9255	1401.8	4.587	4.510	4.445	4.478
0.3802	0.9199	1392.8	4.495	4.286	4.254	4.300
0.5126	0.9002	1385.1	4.623	4.098	4.051	4.101
0.6206	0.8751	1380.2	4.242	3.937	3.873	3.919
0.7104	0.8615	1375.3	4.123	3.798	3.714	3.754
0.7863	0.8502	1345.8	3.945	3.678	3.612	3.645
0.8513	0.8227	1325.8	3.721	3.572	3.437	3.461
0.9075	0.8207	1289.2	3.568	3.478	3.395	3.411
0.9567	0.7798	1250.5	3.242	3.395	3.195	3.203

x_1	ρ_{Exp}/ g.cm^{-3}	$u_{Exp/m.s}$$^{-1}$	Pi_{obs} 10^{-9}Pa	Pi_{Flory} 10^{-9}Pa	Pi_{RS} 10^{-9}Pa	Pi_{Gli}10^{-9}Pa
		Acetonitrile+DMA				
293.15						
0.5562	0.9421	1445.6	4.549	4.131	4.237	4.322
0.6610	0.9159	1429.7	4.379	3.984	4.069	4.147
0.7452	0.8856	1409.8	4.148	3.859	3.876	3.943
0.8144	0.8653	1395.7	3.994	3.751	3.741	3.794
0.8722	0.8529	1370.9	3.799	3.657	3.616	3.655
0.9212	0.8355	1365.8	3.733	3.575	3.541	3.567
0.9634	0.8159	1335.8	3.525	3.502	3.429	3.442
298.15						
0.2453	0.9358	1449.2	4.566	4.477	4.390	4.445
0.4223	0.9256	1435.7	4.454	4.267	4.212	4.288
0.5562	0.9145	1425.6	4.313	4.093	4.026	4.104
0.6610	0.8995	1409.1	4.191	3.946	3.907	3.981
0.7452	0.8755	1389.7	4.014	3.820	3.763	3.826
0.8144	0.8504	1369.7	3.794	3.712	3.589	3.639
0.8722	0.8348	1348.9	3.620	3.618	3.468	3.505
0.9212	0.8119	1335.7	3.481	3.536	3.353	3.377
0.9634	0.7998	1315.1	3.358	3.463	3.285	3.297
303.15						
0.2453	0.9248	1423.9	4.450	4.441	4.306	4.363
0.4223	0.9016	1406.2	4.272	4.229	4.075	4.153
0.5562	0.8908	1390.5	4.154	4.052	3.928	4.010
0.6610	0.8705	1379.8	4.014	3.902	3.763	3.839
0.7452	0.8559	1359.1	3.879	3.775	3.659	3.724
0.8144	0.8391	1336.7	3.695	3.665	3.525	3.578
0.8722	0.8069	1315.8	3.480	3.570	3.360	3.398
0.9212	0.7909	1295.7	3.317	3.486	3.245	3.270
0.9634	0.7854	1280.6	3.259	3.413	3.217	3.230
308.15						
0.2453	0.9158	1408.9	4.476	4.436	4.331	4.390
0.4223	0.9016	1401.9	4.346	4.220	4.099	4.175
0.5562	0.8759	1388.9	4.191	4.041	3.898	3.982
0.6610	0.8669	1375.1	4.082	3.889	3.773	3.851
0.7452	0.8498	1346.9	3.866	3.760	3.623	3.691
0.8144	0.8257	1326.7	3.690	3.649	3.488	3.542
0.8722	0.8067	1302.8	3.504	3.552	3.363	3.403
0.9212	0.7895	1275.3	3.310	3.468	3.247	3.273
0.9634	0.7759	1262.3	3.218	3.393	3.177	3.190
313.15						
0.2453	0.9098	1395.2	4.458	4.451	4.315	4.374
0.4223	0.889	1380.5	4.291	4.231	4.074	4.156
0.5562	0.8759	1365.8	4.175	4.047	3.921	4.006
0.6610	0.8566	1340.5	3.968	3.893	3.750	3.829
0.7452	0.8442	1326.4	3.814	3.761	3.599	3.666
0.8144	0.8198	1309.5	3.653	3.648	3.462	3.516
0.8722	0.7908	1285.4	3.422	3.550	3.295	3.334
0.9212	0.7828	1259.7	3.278	3.464	3.219	3.245
0.9634	0.7742	1241.0	3.164	3.388	3.149	3.162

that associated processes provide fairly good results as compared to non-associated. Higher deviation values in Flory model can be explained as the model was developed for non-electrolyte γ-meric spherical chain molecules and the system under investigation have interacting and associating properties. Moreover, the expression used for the computation of α and β_T[29] are also empirical in nature. Table 4 indicates that with the increase of mole fraction, the values of density, theoretical pseudo-Gruneisen parameters and theoretical internal pressure obtained from all the models decrease at all temperatures.

Excess internal pressure can be defined as;

$$Pi^E = Pi_{mix} - Pi_{idl} \quad ...(20)$$

and$Pi_{idl} = x_1Pi_1 + x_2\, Pi_2$

wherePi^E is the excess internal pressure , $Pi_{idl}$is the ideal internal pressure and Pi_{mix} is internal pressure of liquid mixture respectively.

Variation of excess internal pressure, Pi^E, with composition at various temperatures is presented in Figs 1-4. For excess properties, sign and magnitude are of much important to describe the molecular

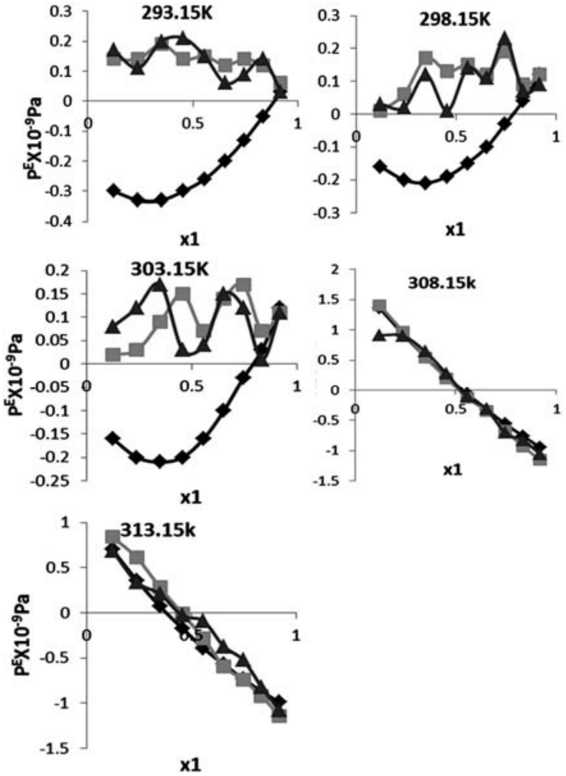

Fig. 1 — Plot of excess internal pressure P^E, with mole fraction x_1 for x acetonetrile + (1−x) formamide; ♦, excess internal pressure from PFP model; ■, excess internal pressure RS model; ▲, excess internal pressure from Glinski model.

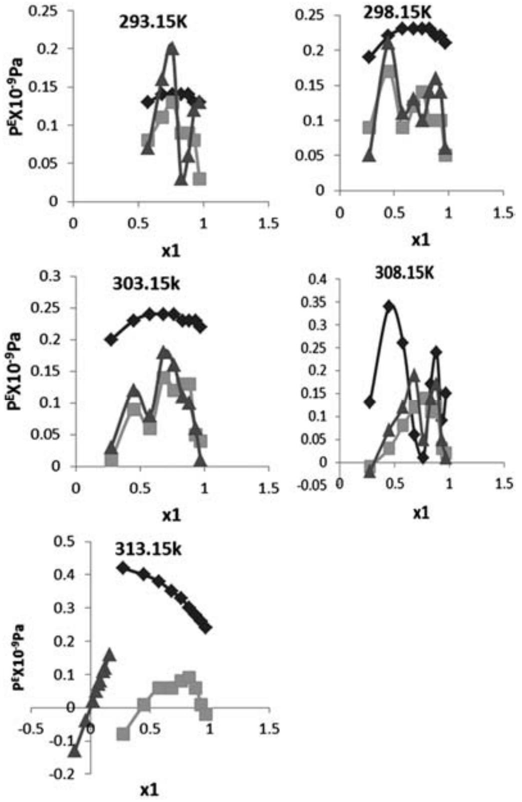

Fig. 2 — Plot of excess internal pressure P^E, with mole fraction x_1 for x acetonitrile + (1−x) NMA;♦, excess internal pressure from PFP model; ■, excess internal pressure RS model; ▲, excess internal pressure from Glinski model.

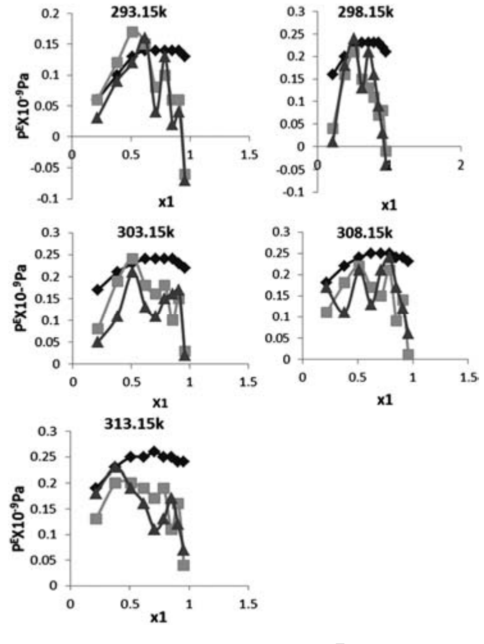

Fig. 3 — Plot of excess internal pressure P^E, with mole fraction x_1 for x acetonitrile + (1−x) DMF;♦, excess internal pressure from PFP model; ■, excess internal pressure RS model;▲, excess internal pressure from Glinski model.

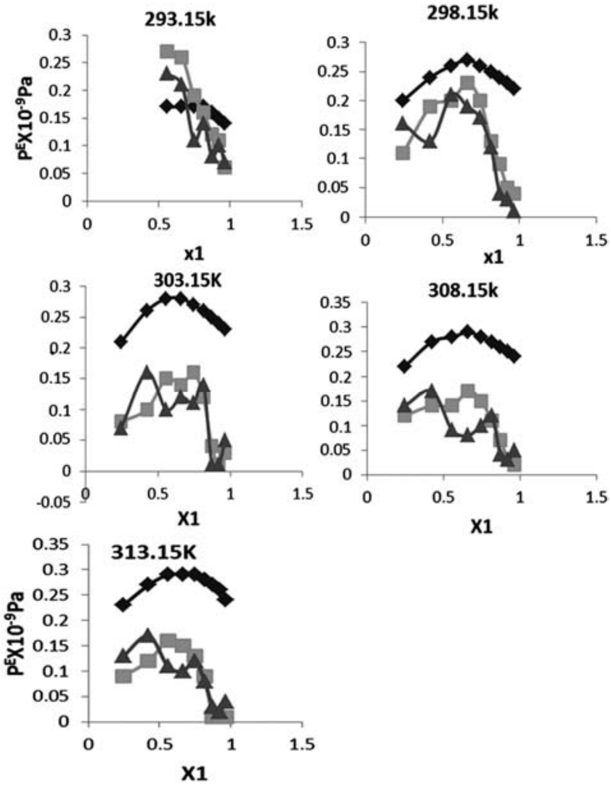

Fig. 4 — Plot of excess internal pressure P^E, with mole fraction x_1 for x acetonitrile+ (1−x) DMA;♦, excess internal pressure from PFP model; ■, excess internal pressure RS model;▲, excess internal pressure from Glinski model.

interactions involved in the liquid system. A care full look in all the figures indicates that no regular trends are observed for excess internal pressure. Negative values of Pi^E show the strong molecular interactions between the liquid components. Dispersion type interactions and structural effects arising from interstitial accommodation because of differences in molecular volumes and free volumes between liquid components contribute negative terms to Pi^E. The repulsive forces between the loan pair of electrons leads to positive values of Pi^E suggest the presence of weak interactions between the component molecules and the favoring packing of unlike molecules.

Conclusion

Conclusively, models assuming associated processes give more reliable results as compared to non-associated processes and helpful in deducing the internal structure of associates through the fitted values of pseudo-Gruneisen parameter and internal pressure in a hypothetical pure associate and observed dependence of concentration on composition of a mixture.

Acknowledgement

Authors are very thankful to U.G.C., New Delhi for financial support (Grant-34-332/2008(SR), 15-57/12(SA-II) and Department of Chemistry, V.S.S.D.College, for cooperation.

References

1 Hildebrand J H & Scott R L, *The Solubility of Non-Electrolytes*, 3rd Edn (Dover Publication, New York, NY), 1964.
2 Dack M R J, *Aust J Chem*, 28 (8) (1975) 1643.
3 Grant-Taylor David F & Macdonald Digby D, *Can J Chem*, 54 (17) (1976) 2813.
4 Macdonald Digby D & Hyne J B, *Can Chem*, 49 (4) (1971) 611.
5 Pandey J D, Tripathi N & Dey R, *Ind J Phys*, 70B (2) (1996) 147.
6 Sharma B K, *Acoust Soc Am*,73 (1983) 106.
7 Pandey J D, Singh A K &Dey Ranjan, *Pramana J Phys*, 64 (1) (2005) 135.
8 Dey Ranjan, Singh A K & Pandey J D, *J MolliqLiq*, 124 (2006) 121.
9 Subrahmanyam S V, Ramanujappa T & Rajgopal E S, *Acustica*, 52 (1983) 125.
10 Shukla R K & Kumar Atul, *Acta Chim Solv*, 55 (3) (2008) 627.
11 Shukla R K, Shukla Shailendra, Pandey Vivek & Awasthi Piyush, *J Phys Chem Liq,* 45 (2) (2007) 169.
12 Jain Pragati & Singh Mukhtar, *J Chem Eng Data*, 49 (2004) 1214.
13 Pandey J D, Soni N K, Day R O &Verma Richa, *Fluid Phase Equil,* 15 (2004) 17.
14 Knopoff L & Shapiro J N, *Phys Rev*, B1 (1970) 3893.
15 Shukla R K, Shukla S K, Pandey V K & Awasthi Piyush, *J Molliq Liq*, 137 (2008) 104.
16 Shukla R K, Kumar Atul, Srivastava Kirti, Gupta Sanjay & Yadav Shilpi, *J Molliq Liq*, 140 (2008) 25.
17 Pandey J D & Day Ranjan, *Acous Lett*, 24 (2000) 105.
18 Pandey J D, Dubey G P, Day R &Dubey S N, *Acta Acustica*, 83 (1997) 90 .
19 Pandey J D & David Alec D M, *J Chem Phys,* 77 (1982) 1064.
20 Pandey J D, Shukla A K, Tripathi Neelima & Dubey G P, *Pramana J Phys*,40 (2) (1993) 1.
21 Shukla R K, Kumar Atul, TomarNagendra, Srivastava Urvashi & SrivastavaKirti, *Int J Thermo Phy,* accepted 2014.
22 Abe A & Flory P J, *J Am ChemSoc*, 82 (1965) 1838 .
23 Flory P J Orwoll R A &Vrij A, *J Am Chem Soc*, 86 (1964) 3515.
24 Ramaswamy K & Anbananthan D, *Acustica*, 48 (1981) 281.
25 Glinski J, *J ChemPhys*, 118 (2003) 2301.
26 Redlich O & Kister A T, *Ind Eng Chem*, 40 (1948) 345.
27 Natta G & Baccaredda M, *Atti Accad NazLincei*, 4 (1948) 360.
28 Shukla R K, Awasthi N, Kumar A, Shukla A &Pandey V K, *J Molliq Liq*, 158 (2011)131.
29 Pandey J D &Verma Richa, *Chem Phys*, 270 (2001) 429.
30 Riddick A Bunger W B & Sakano T K, *Organic Solvents Techniques of Chemistry*, 4th Edn (Willey New York), 1986.