SHORT PAPER

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Application of Flory's Statistical Theory for the estimation of internal pressure of the liquid mixtures[†]

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Flory's Statistical Theory has been employed for the evaluation of internal pressure of liquid mixtures at varying conditions. The method used for the evaluation does not use any empirical relation, unlike the approaches of previous workers. The computed values have been compared against the values obtained from thermodynamic relation taken as an experimental method. To the best of our knowledge, the present approach has not been employed previously by any worker. The excellent agreements between the computed and experimental values prove the applicability of this approach for the evaluation of internal pressure in liquid mixtures.

Keywords: Flory's Statistical Theory, internal pressure, thermal expansivity, interaction parameter

Internal pressure is a fundamental liquid property, which is a resultant of forces of attraction and repulsion between the constituents of liquids. As degree of cohesion differs from liquids to liquids, internal pressure provides useful information about the molecular interactions in the liquid systems. Richards[1], Dack[2] and Hildebrand and Scott[3-4] recognised the importance of this property in liquids. Internal pressure has gained enormous amount of interest by chemists, physicists and chemical engineers, as it provides a measure of explaining molecular interactions, internal structure, clustering phenomenon, ionic interactions, dipolar interactions and surface tension. Various relations for the estimation of internal pressure in liquids have been proposed.[5-8] Studies by some workers[9-16] on the various other parameters of liquids have turned to be very useful in the extension of studies on internal pressure. Barton[17,18] explained extensively about internal pressure and its related parameters of the liquid state. Internal pressure and related parameters in liquids and liquid mixtures have been evaluated by various workers,[19-29] using various relations. Pandey[21] evaluated internal pressure in various liquid mixtures with the aid of surface tension data computed using Flory's Statistical Theory.[13-16] Pandey *et al.*[22] evaluated internal pressure in organic liquids mixtures using the method of Buehler et al[5,6] in conjunction with a hard-sphere model. Buehler's [5,6] method for evaluation of internal pressure was also utilized by other workers.[23-25] Sachadeva *et al*[26] utilised thermodynamic relationships to evaluate the internal pressure in paraffins. Pandey et al[27] evaluated internal pressure in molten salts utilising Flory's Statistical Theory[13-16] to compute ultrasonic velocity and Auerbach's empirical relation[12] to compute surface tension. Suryanarayana[7,8] utilised the free volume concept in conjunction with viscosity to formulate an empirical relation for the estimation of internal pressure of liquids. The relation has also been utilised to evaluate internal pressure in liquids, by other workers.[28-29]

In the present work, a new approach for the estimation of internal pressure of liquid mixtures based upon Flory's Statistical Theory[13-16] has been attempted and analysed. In this approach, the necessary parameters, thermal expansivity (α) and isothermal compressibility (β_T) of liquid mixtures at a given composition, have been evaluated using the relations based on the Flory's Statistical Theory and these parameters have been then utilised to evaluate internal pressure. This method is quite comprehensive, as the method requires the α and β_T values of *pure liquids only* as input parameters. Though Flory's Statistical Theory has been utilised by previous workers also, the present approach does not apply any empirical relation, unlike the previous studies. To the best of our knowledge, this approach of using the Flory's Statistical Theory completely, *i.e.* without the use of any empirical relation, has not been attempted previously. The present approach is likely to give very good results due to the inclusion of the interaction parameter clearly in the Flory relations. For comparison only, some other relations have been utilised to evaluate the internal pressure in some pure organic liquids.

Theoretical

The thermodynamic relationship among isothermal compressibility (β_T), thermal expansivity (α) and internal pressure (P_i) is given as:

$$P_i = \frac{\alpha\, T}{\beta_T} \tag{1}$$

From studies on free volume[7-10], Suryanarayana[8] proposed the following relation for the evaluation of internal pressure in liquid systems from the knowledge of viscosity (η), density (ρ),sound velocity (u) and molar mass (M):

$$P_i = bRT\left(\frac{k\eta}{u}\right)^{1/2}\frac{\rho^{2/3}}{M^{7/6}} \tag{2}$$

where, $b = 2$, $k = 4.28 \times 10^9$, η is in poise, u is in cm/s and ρ is in g/cm^3.

Based upon the equation of the state due to Buehler *et al.*,[5,6] the internal pressure can be related to molar volume (V), absolute temperature (T), molecular diameter (d), Avogadro's number (N) and the universal gas constant (R) as:

$$P_i = \frac{2^{1/6}\,RT}{2^{1/6}\,V - d N^{1/3} V^{2/3}} \tag{3}$$

The molecular diameter required for eqn (3) can be computed using the relation:[11]

$$d = \left(\frac{V\sigma^{1/4}}{7.2\times 10^{19}\, T_c^{1/4}}\right)^{2/5}$$

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where, σ is surface tension and T_c is the critical temperature. The surface tension (σ) can be calculated using the following relation:[12]

$$\sigma = 6.3 \times 10^{-4} \rho u^{3/2}$$

where, ρ is in g/cm^3 and u is in m/s.

As a new approach, the internal pressure of liquid mixtures at the given composition can be deduced using the relation

$$P_i = \frac{(\alpha)_{Flory} \mathrm{T}}{(\beta_T)_{Flory}} \qquad (4)$$

where, $(\alpha)_{\mathrm{Flory}}$ and $(\beta_T)_{\mathrm{Flory}}$ are the thermal expansivity and isothermal compressibility of liquid mixtures, computed using Flory's Statistical Theory, from knowledge of the α and β_T of pure liquids. If the thermal expansivity (α) and isothermal expansivity (β_T) of pure liquid components are known, the values of α and β_T for a liquid mixture of a given composition can be evaluated using the relations:

$$(\alpha)_{Flory} = \frac{3(\tilde{V}^{1/3} - 1)}{[1 - 3(\tilde{V}^{1/3} - 1)]T}$$

and

$$(\beta_T)_{Flory} = \frac{(\alpha)_{Flory}\, T\, \tilde{\mathrm{V}}^2}{P^*}$$

In the above equations, $\tilde{V}$ is the reduced volume and P^* is the characteristic pressure the liquid mixture, which is given by

$$P^* = T^* \sum \frac{\psi_i P_i^*}{T_i^*}$$

where, Ψ_i, P_i^* and T_i^* are the site fraction, characteristics pressure and characteristic temperature of the pure components of liquid mixtures, and T^* is the characteristic temperature of the liquid mixture. The relations for the computation of the parameters like Ψ_i, P_i^*, T_i^*, T^*, V^*, $\tilde{V}$, $\tilde{T}$ and the interaction parameter (X_{ij}) required for the above relations have been discussed by previous workers.[15,30] The present approach is supposed to provide a novel method for the evaluation of the internal pressure in the liquid mixtures, as it uses the minimum input data like α, β_T and molar volume only of pure components.

Results and discussion

The equations (1 – 3) have been utilised for the computation of internal pressure of some pure liquids and the results have been depicted in Table 1. The Eqn (4) has been utilised to evaluate the internal pressure of the some liquid mixtures at various conditions and the results have been depicted in Tables 2 and 3. The necessary data for computation have been taken from the literature.[31-33]

Closer perusal of Table 1 shows that Eqns (2 and 3) do not provide satisfactory results in most of the cases. The possible reason for the type of deviations in these methods could be that the relations are derived based upon some adjustments and the approaches use more than one empirical relation. This shows that these equations in the present forms cannot be recommended strongly in most of the cases under investigation. The deviations in results from Eqn (2) reflect

Table 1 Internal pressure of various pure liquids at 303.15 K

	ρ	u	$\alpha/10^{-3}$	$\beta_T/10^{-11}$	$\eta/10^{-3}$	$P_i/10^5$	% Dev. in P_i	
Compounds	kg/m^3	m/s	K^{-1}	m^2/N	N s/m^2	N/m^2	Eqn 2	Eqn 3
Benzene	867.7	1278	1.320	102.7	0.5802	3896	–1.62	23.39
Cyclohexane	766.2	1230	1.239	119.9	0.8016	3133	–27.76	23.30
Dioxane	1018.5	1325	1.115	78.7	1.0678	4294	–18.76	19.55
Toluene	853.9	1285	1.065	96.0	0.5365	3363	7.87	24.84
Chlorobenzene	1095.7	1250	0.990	78.9	0.7223	3804	10.47	26.24
Chloroform	1466.5	967	1.300	108.6	0.6058	3629	–10.66	–4.19

Table 2 Internal pressure and related parameters of binary liquid mixture: cyclohexane (**1**) + cyclohexanol (**2**)

					$(\mathrm{Pi})_{\mathrm{Flory}}$ and related properties				
T K	x_2	$\alpha/10^{-3}$ K^{-1}	$\beta_T/10^{-11}$ m^2/N	Pi/10^5 N/m^2	$\tilde{V}/10^{-6}$ m^3/mol	$(\alpha)_{\mathrm{Flory}}/10^{-3}$ K^{-1}	$(\beta_T)_{\mathrm{Flory}}/10^{-11}$ m^2/N	Pi/10^5 N/m^2	% Dev.
298.15	0.0000	1.215	112.77	3212	1.290	1.215	112.77	3212	0.00
	0.1977	1.128	102.90	3268	1.270	1.110	97.82	3383	–3.51
	0.3178	1.077	93.10	3449	1.259	1.054	90.08	3489	–1.15
	0.4185	1.047	88.00	3547	1.250	1.010	84.25	3574	–0.76
	0.5050	1.018	83.40	3639	1.242	0.974	79.66	3645	–0.17
	0.6828	0.968	74.20	3890	1.228	0.907	71.26	3795	2.44
	0.7871	0.911	68.70	3954	1.221	0.871	66.90	3882	1.82
	0.9001	0.860	63.60	4032	1.213	0.835	62.58	3978	1.32
	1.0000	0.804	59.07	4058	1.206	0.804	59.07	4058	0.00
313.15	0.0000	1.265	128.97	3072	1.311	1.265	128.97	3072	0.00
	0.1977	1.145	115.80	3096	1.289	1.150	110.50	3259	–5.25
	0.3178	1.098	105.00	3275	1.276	1.088	101.10	3370	–2.91
	0.4185	1.064	98.40	3386	1.266	1.041	94.08	3465	–2.33
	0.5050	1.034	92.20	3512	1.259	1.003	88.61	3545	–0.93
	0.6828	0.973	81.60	3734	1.243	0.931	78.69	3705	0.78
	0.7871	0.927	75.80	3830	1.235	0.893	73.60	3799	0.79
	0.9001	0.875	70.00	3914	1.226	0.855	68.59	3904	0.28
	1.0000	0.823	64.55	3993	1.219	0.823	64.55	3993	0.00

Table 3 Internal pressure and related parameters of binary liquid mixture: acetone **(1)** + methyl iodide **(2)**

					$(\mathrm{Pi})_{\mathrm{Flory}}$ and related properties				
T K	x_1	$\alpha/10^{-3}$ K^{-1}	$\beta_T/10^{-11}$ m^2/N	Pi/10^5 N/m^2	$/10^{-6}$ m^3/mol	$(\alpha)_{\mathrm{Flory}}$ 10^{-3} K^{-1}	$(\beta_T)_{\mathrm{Flory}}$ 10^{-11} m^2/N	Pi/10^5 N/m^2	% Dev.
253.20	0.0000	1.167	72.05	4101	1.246	1.167	72.05	4101	0.00
	0.2000	1.269	78.86	4074	1.252	1.201	75.64	4020	1.33
	0.4000	1.298	83.20	3950	1.257	1.234	79.27	3942	0.22
	0.6000	1.314	86.36	3853	1.263	1.267	82.94	3868	–0.40
	0.8000	1.324	88.72	3779	1.269	1.300	86.65	3799	–0.53
	1.0000	1.332	90.40	3731	1.274	1.332	90.40	3731	0.00
263.20	0.0000	1.184	77.57	4017	1.257	1.184	77.57	4017	0.00
	0.2000	1.277	84.58	3974	1.263	1.216	81.39	3932	1.04
	0.4000	1.310	89.51	3852	1.268	1.249	85.25	3856	–0.11
	0.6000	1.326	93.07	3750	1.274	1.281	89.16	3782	–0.84
	0.8000	1.335	95.53	3678	1.279	1.312	93.11	3709	–0.83
	1.0000	1.344	97.11	3643	1.285	1.344	97.11	3643	0.00
273.20	0.0000	1.200	83.40	3931	1.268	1.200	83.40	3931	0.00
	0.2000	1.282	90.70	3862	1.274	1.232	87.67	3839	0.58
	0.4000	1.316	95.93	3748	1.279	1.265	92.02	3756	–0.21
	0.6000	1.333	99.98	3642	1.285	1.297	96.44	3674	–0.87
	0.8000	1.347	103.13	3568	1.291	1.329	100.94	3597	–0.80
	1.0000	1.361	105.50	3524	1.296	1.361	105.50	3524	0.00
283.20	0.0000	1.214	89.51	3841	1.278	1.214	89.51	3841	0.00
	0.2000	1.292	97.01	3772	1.284	1.247	94.27	3746	0.68
	0.4000	1.323	103.13	3633	1.290	1.280	99.13	3657	–0.65
	0.6000	1.342	107.87	3523	1.296	1.314	104.08	3575	–1.48
	0.8000	1.361	111.52	3456	1.302	1.347	109.14	3495	–1.13
	1.0000	1.380	114.29	3420	1.308	1.380	114.29	3420	0.00
293.20	0.0000	1.229	95.83	3760	1.289	1.229	95.83	3760	0.00
	0.2000	1.300	103.92	3668	1.295	1.263	101.16	3661	0.20
	0.4000	1.332	110.93	3521	1.301	1.296	106.63	3564	–1.22
	0.6000	1.355	116.46	3411	1.308	1.330	112.23	3475	–1.85
	0.8000	1.377	120.90	3339	1.314	1.364	117.98	3390	–1.51
	1.0000	1.398	123.86	3309	1.320	1.398	123.86	3309	0.00

the need for re-evaluating the value of especially the factor '*b*' used in this equation, which is usually taken as '2'. However, this method can be considered as an alternative and convenient method, when only viscometric, volumetric and ultrasonic data are available. Tables 2 and 3 enlist the experimental values of α, β_T and P_i along with their values as computed using Flory's Statistical Theory. As expected while aiming the present study, Flory's Theory is found to give excellent results. The values of α and β_T as computed using Flory's Statistical Theory (column 7 and 8 of Tables 2 and 3) also show good agreement with the experimental values for the same. The very low percentage differences in internal pressure (column 10 of Tables 2 and 3) prove the applicability of the Flory's Statistical Theory for the evaluation of internal pressure of the liquid mixtures. The present study can also be considered as an authentication for the method of computing internal pressure using Flory's Statistical Theory completely *i.e.* without the use of any empirical relation.

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