Comments on 'Prediction of internal pressure of binary liquid mixtures using Flory's statistical theory'

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A. Ali and M. Tariq (*J. Chem. Res.*, 30, 2006, 261) have reported the prediction of internal pressure of binary liquid mixtures using Flory's statistical theory. It is now shown that the Ali–Tariq approach to calculate thermal expansion coefficient α_p and isothermal compressibility κ_T for both organic liquids and liquid mixtures, is totally wrong, misleading and introduces errors in thermodynamic data. It should also be emphasised that once the correct expressions for calculating Flory's interaction parameter X_{12} are known, one should use only those expressions to derive X_{12} in the prediction of any thermodynamic property of liquid mixtures.

Keywords: binary mixtures, Flory's statistical theory, thermal expansion coefficient, thermodynamic data

In their report on the 'Prediction of internal pressure of binary liquid mixtures using Flory's statistical theory', Ali and Tariq[1] calculated the so-called experimental internal pressure ($\pi_{int(exp)}$) of liquid mixtures using so-called experimentally-evaluated thermal expansivity ($\alpha_{P(exp)}$) and isothermal compressibility ($\beta_{T(exp)}$ or $\kappa_{T(exp)}$) for 13 binary liquid mixtures involving a variety of components. These properties, at one atmospheric pressure, were calculated by use of the following relationships:

$$\pi_{int(exp)} = \alpha_{P(exp)}.T/\kappa_{T(exp)} \tag{1}$$

$$\alpha_{P(exp)} = (0.0191\kappa_{T(exp)})^{1/4} \tag{2}$$

$$\kappa_{T(exp)} = 1.71 \times 10^{-4}/(T^{4/9}\,u^2\,\rho^{4/3}) \tag{3}$$

where u and ρ are the experimentally-determined speed of sound and density of pure components or mixtures respectively. In fact, the calculated properties α_P, κ_T and π_{int} are empirical rather than experimental. In no case is it justified to call them experimental. Therefore, henceforth, we shall denote calculated properties from Eqns (1)–(3) as empirical (emp) ones.

Furthermore, applying Flory's statistical theory,[2,3] Ali and Tariq[1] computed the internal pressure ($\pi_{int,Flory}$) using the derived empirical thermal expansion coefficient (α_P) and isothermal compressibility (κ_T). The results were reported in Tables 1 and 2 of ref.1. Discussion is based on the basis of comparison of empirical internal pressure ($\pi_{int,emp}$), with those computed from the Flory theory ($\pi_{int,Flory}$), reported in terms of average percentage deviations (APD). Taking into account the values of APD, the authors claimed the validity of what was called "their entirely new approach".

It is always a significant and important step to develop a theoretical approach to predict internal pressure (also known as the cohesion pressure or energy-volume coefficient), an interesting and valuable thermodynamic property that describes the macroscopic result of molecular interaction,[4,5] as its direct determination is not very convenient. It is usual that any new predictive method should be tested by the measurement of adequate accuracy and precision, as has been adopted by Dzida[6] in the description of internal pressure (π_{int}) of six mixtures comprising of nonpolar components through the Flory model.[2,3]

For an approach such as described by Ali and Tariq[1], several points need to be considered. First (i), the validity of Eqns (2) and (3) to determine α_P and κ_T of pure components and binary liquid mixtures and use of α_P and κ_T to further determine π_{int}.

Table 1 Comparison between the values of $\alpha_P/10^{-3}K^{-1}$, $\kappa_T/10^{-11}$ cm^2 dyn^{-1} and π_{int}/MPa reported by Ali and Tariq[1] and reliable experimental values

	From ref. 1			Eqn (1)	From literature		Eqn (1)	% Deviations* In		
	T/K	$\alpha_{P(emp)}$	$\kappa_{T(emp)}$	$\pi_{int(emp)}$	$\alpha_{P(exp)}$	$\kappa_{T(exp)}$	$\pi_{int(exp)}$	α_P	κ_T	π_{int}
DMSO	298.15	1.010	5.452	552.3	0.911[a]	5.26[b]	516.8	−10.9	−3.7	−6.9
Ethanol	298.15	1.281	14.116	270.6	1.100[c]	11.53[d]	284.4	−16.5	−22.4	4.9
	303.15	1.291	14.540	269.2	1.110[c]	11.89[d]	283.0	−16.3	−22.3	4.9
Acetonitrile	298.15	1.219	11.570	314.1	1.388[a]	10.70[e]	386.8	12.2	−8.1	18.8
	303.15	1.228	11.910	312.6	1.398[a]	11.20[e]	378.4	12.2	−6.3	17.4
DMF	303.15	1.075	6.986	466.5	0.765[a]	5.996[f]	386.8	−40.5	−16.5	−20.6
THF	308.15	1.191	10.520	348.9	1.281[g]	10.80[h]	365.5	7.0	2.6	4.6
Benzene	308.15	1.184	10.298	354.3	1.244[i]	10.44[i]	367.2	4.8	1.4	3.5
2,2,4-Trimethyl-pentane	308.15	1.407	20.530	211.2	1.246[J]	16.71[k]	230.3	−12.9	−23.2	8.3
Cyclohexane	308.15	1.257	13.067	296.4	1.249[i]	12.19[i]	315.7	−0.6	−7.2	6.1
1-Pentanol	308.15	1.219	11.549	325.3	0.944[c]	9.35[d]	311.1	−29.1	−23.5	−4.5
1-Hexanol	298.15	1.288	10.446	367.6	0.908[c]	8.36[d]	323.8	−41.9	−25.0	−13.5
	303.15	1.202	10.921	333.7	0.915[c]	8.61[d]	322.2	−31.4	−26.8	−3.6
	308.15	1.203	10.967	338.0	0.923[c]	8.95[d]	317.8	−30.3	−22.5	−6.4
1-Heptanol	308.15	1.191	10.516	349.0	0.892[c]	8.50[d]	323.4	−33.5	−23.7	−7.9
1-Octanol	308.15	1.176	10.022	361.6	0.883[c]	8.22[d]	331.0	−33.2	−21.9	−9.2
1-Decanol	308.15	1.163	9.580	374.1	0.855[c]	7.75[d]	340.0	−36.0	−23.6	−10.0

*%deviation = 100 $(X_{exp}-X_{emp})/X_{exp}$, where X = α_P, κ_T, and π_{int}.

[a]Ref. 8; [b]derived from Eqn (9) using u, α_P, C_P, Vm data from refs 8,9; [c]derived from density data ref. 10; [d]ref. 10; [e]ref. 11, [f]derived from Eqn (9) using u, α_P, C_P, Vm data from refs 8,12; [g]ref. 13; [h]derived from Eqn (9) using u, α_P, C_P, Vm data from refs 8,13; [i]ref. [14]; [j]derived from density data ref. 15; [k]derived from Eqn (9) using u, α_P, C_P, Vm data from refs 15,16.

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Table 2 Comparison between experimental α_P, κ_T, and π_{int} and those obtained using Eqns (1) to (3) at different temperatures (T) and pressures (P)

liquids			Experimental values[17–23]			using Eqns (1) to (3)*			% deviations in		
	T K	P MPa	α_P kK^{-1}	κ_T TPa^{-1}	π_{int} MPa	α_P kK^{-1}	κ_T TPa^{-1}	π_{int} MPa	α_P	κ_T	π_{int}
2-Methyl-1-butanol	298.15	0.1	0.918	908	301.4	1.214	1137	318.3	–32.2	–25.2	–5.6
	308.15	0.1	0.950	969	302.1	1.230	1199	316.2	–29.5	–23.7	–4.7
	318.15	0.1	0.984	1035	302.5	1.247	1268	313.1	–26.8	–22.5	–3.5
	298.15	10	0.865	821	314.1	1.184	1027	343.5	–36.8	–25.1	–9.3
	298.15	50	0.723	609	354.0	1.099	763	429.4	–52.0	–25.3	–21.3
	298.15	100	0.615	469	391.0	1.029	587	522.7	–67.3	–25.1	–33.7
1-Heptanol	298.15	0.1	0.858	807	316.7	1.178	1007	348.6	–37.3	–24.8	–10.1
	298.15	100	0.599	445	401.0	1.015	555	545.0	–69.5	–24.7	–35.9
	318.15	100	0.617	476	412.0	1.026	579	563.1	–66.3	–21.7	–36.7
1-Decanol	298.15	0.1	0.830	739	335.1	1.151	920	373.0	–38.7	–24.6	–11.3
	298.15	70	0.623	479	388.0	1.029	587	522.8	–65.1	–22.6	–34.7
	318.15	70	0.643	518	395.2	1.043	618	536.3	–62.1	–19.5	–35.7
Cyclohexane	293.15	0.1	1.185	1089	318.6	1.222	1169	306.4	–3.2	–7.3	3.8
	303.15	0.1	1.223	1171	316.4	1.247	1267	298.3	–2.0	–8.2	5.7
	313.15	0.1	1.266	1292	306.8	1.274	1378	289.2	–0.6	–6.7	5.7
	323.15	0.1	1.297	1399	299.4	1.303	1508	279.0	–0.5	–7.8	6.8
	333.15	0.1	1.331	1520	291.6	1.397	1646	233.4	–0.1	–8.3	7.6
n-Hexane	298.15	0.1	1.385	1669	247.3	1.409	2061	203.7	–1.7	–23.5	17.6
n-Octane	298.15	0.1	1.158	1282	269.2	1.321	1597	246.5	–14.1	–24.5	8.4
n-Decane	298.15	0.1	1.050	1094	286.0	1.271	1367	277.0	–21.0	–25.0	3.1
n-Dodecane	298.15	0.1	0.980	988	295.6	1.238	1231	299.7	–26.3	–24.6	–1.4
n-Tetradecane	298.15	0.1	0.906	910	296.7	1.215	1140	317.6	–34.1	–25.3	–7.0
n-Hexadecane	298.15	0.1	0.884	857	307.4	1.196	1071	332.8	–35.3	–25.0	–8.3

* u and ρ were taken from Refs. 17–23.

Second (ii), the selection of the 13 mixtures under investigation, involving either one or both of the components being polar or highly polar with specific interactions between them, to examine the Flory theory[2,3] in order to predict π_{int}. Third (iii), the manner in which Flory's contact interaction parameter[2] X_{12} [Eqn (4)] was evaluated for the binary mixtures under consideration to evaluate theoretically the internal pressure.

$$X_{12} = P_1^*[1-(P_2^*/P_1^*)^{1/2}(V_2^*/V_1^*)^{1/6}]^2 \tag{4}$$

The notations used in Eqn (4) are same as used by Flory.[2,3]

Pure components

For the calculation of π_{nt}, in the paper under consideration,[1] Table 1 lists the α_P, and κ_T values of involved pure components obtained through Eqns (2) and (3), using speed of sound u and density ρ measured in the authors' laboratory (references cited in ref. 1). All of the published data that we have found in the available literature (included in Table 1), indicated that the $\alpha_{p(emp)}$ and $\kappa_{T(emp)}$ values differ strongly from the experimental values and those obtained through the use of thermodynamic relationships.[7] Percentage deviations as large as 41.9%, 26.8% and 20.6% from the reliable $\alpha_{P(exp)}$, $\kappa_{T(exp)}$ and $\pi_{int(exp)}$, respectively, with average percentage deviations 23.9% in α_P, 19.2% in κ_T, and 3.9% in π_{int} are observed in the case of the pure components under investigation.[1] These deviations tend to further increase if the study is undertaken at higher pressures and temperatures (Table 2). Thus, Eqns (2) and (3) are not suitable for the calculation of α_P and κ_T even for the pure liquid components, and hence π_{int}.

Binary liquid mixtures

The internal pressure is defined thermodynamically[24]

$$\pi_{int} = (\partial U/\partial V)_T = T.\,(\partial p/\partial T)_V - p \tag{5}$$

where U is the internal energy, p is the external pressure, and $(\partial \rho/\partial T)_V = \alpha p/\kappa_T$. The $(\partial \rho/\partial T)_V$ term is frequently called the isochoric thermal pressure coefficient γ. At low external pressure p, expression (5) reduces to the same as Eqn (1)

$$\pi_{int} = \alpha p \cdot T/\kappa_T \tag{6}$$

Apart from the so-called direct method (the measurement of isochoric thermal pressure coefficients), π_{int} can be determined from direct or indirect measurements[25] of κ_T. One convenient and well-established method for the determination of κ_T (and as a result, π_{int}) is the well-known acoustic method.[26]

We determined $\alpha_{p(exp)}$ and $\kappa_{T(exp)}$ from standard thermodynamic relations,[7] in order to check the validity of the empirical relations (2) and (3), for the liquid mixtures. The α_P data were determined from volume or density data as a function of temperature using standard relations (7) and/or (8).

$$\alpha_P = -\rho^{-1}(\partial\rho/\partial T)_p \text{ or } V^{-1}(\partial V/\partial T)_p \tag{7}$$

$$\alpha_P = (1/V_m)\left[\sum (x_i\, M_i)\,\alpha^*_{P,i}/\rho^*_i + (\partial V^E_m/\partial T)_{P,x}\right] \tag{8}$$

Similarly, κ_T were determined by the acoustic method[26] from the speed of sound and density data coupled with isochoric heat capacity (C_P) employing the thermodynamic relation (9).

$$\kappa_T = (u^2\rho)^{-1} + \alpha_p^2 V_m T.C_P^{\;-1} \tag{9}$$

Out of 13 liquid mixtures considered in paper [1], analysis on 11 of them is presented here. The required densities or excess molar volumes at different temperatures, and speeds of sound and isochoric heat capacities (C_P) or their excess values (C_P^E) were taken from the work of the present authors[9,12,27–29] and from the literature.[11,30–40] In the absence of direct experimental C_P^E data, these were derived from the temperature coefficients of excess molar enthalpy ($C_P^E = \Delta H^E/\Delta T$). We could not find α_p or α_P^E for the acetonitrile + DMF mixture. In the absence of α_P^E for this mixture, it was assumed to be zero and α_p was calculated as[41]

$$\alpha_p = \phi_1\alpha_{p,1} + \phi_2\alpha_{p,2} \tag{10}$$

where ϕ_i is the volume fraction.

Using these indirect experimental values of α_p and κ_T, the π_{int} were calculated through Eqn (6). Comparison in terms of APD of these α_p, κ_T, and π_{int} values with those derived from Ali and Tariq's[1] approach has been made in Table 3, taking into account all the data points. The APD in α_p and κ_T values calculated by Ali and Tariq[1] are in the range from 13.7 to 26.0% and from 12.2 to 22.7%, respectively, from the true experimental data. The discrepancy in π_{int} is in the range 2.5 to 4.9%. Thus, the approach of Ali and Tariq[1] is erroneous, invalid and misleading for the mixtures too, especially in the determination of α_p and κ_T. We have also calculated Flory's reduction parameters, P* and V*, for pure components and mixtures from both the set of α_p and κ_T [one from Eqns (2) and (3), authors' values[1] and from the thermodynamic Eqns (7) to (9)]. Differences of up to 5.4% in V* and 34% in P* were observed. Thus, use of unrealistic values of α_p and κ_T, also leads to incorrect values of Flory's reduction parameters for pure components as well as for the mixtures, hence thermodynamic properties.

Ali and Tariq[1] refer to ref.42 for Eqns (2) and (3), which is also strictly devoted to the calculation of π_{int} and claimed that "the expressions [Eqns (2) and (3)] are, in practice, appropriate for the calculation of π_{int} in four binary, four ternary and three quaternary organic liquid mixtures". They further claimed that "the empirical relations (2) and (3) were tested for a number of liquid mixtures, including pure liquids, binary, ternary, and quaternary liquid mixtures." However, it is clear from the analysis of Tables 1 to 3 that large deviations/discrepancies were found in the calculated α_P and κ_T for neat liquids and mixtures from the Eqns (2) and (3) and the true experimental values. Even for non-polar liquids alkanes (hexane to hexadecane), deviations of 1.7 to 35.3% in α_p and of 23.5 to 25.0% in κ_T at 298.15 (Table 2) were observed. Thus, one cannot claim that Eqns (2) and (3) are applicable to non-polar liquid components. Thus, observed discrepancies between the experimental [Eqns (7)–(9)] and empirically calculated [Eqns (2) and (3)] values of α_p and κ_T (Tables 1 to 3) also clearly invalidate the claim of Pandey *et al.*[42] to determine α_p and κ_T from Eqns (2) and (3) and hence, computation of π_{int} cannot be considered reliable. Additionally, Pandey and co-workers[43–46] continue to use these unreliable and unacceptable values of α_p and κ_T derived from empirical relations (2) and (3) to further calculate several thermodynamic, acoustic and physical properties, which is not appropriate and will mislead readers less experienced in thermodynamics of liquid mixtures.

Now coming to point (ii), the selection of mixtures in the paper under consideration[1] on which to apply the Flory statistical theory, it is well known that the Flory statistical theory[2,3] as been developed and applied mostly to mixtures involving non-polar components where specific interactions are non-existent.[6,47] In the paper under-consideration, the Flory statistical theory has been applied to estimate π_{int} of thirteen binary mixtures involving polar components where specific interactions exist (except in 2,2,4-trimethylpentane + cyclohexane), which is unjustified and the discussion on results of internal pressure is inappropriate and misleading.

The Flory contact interaction parameter X_{12} (point iii) was calculated using Eqn (4), which is also invalid for the mixtures under investigation. Eqn (4), relating contact interaction parameter, was derived by adoption of the familiar Berthelot relationship[7] for homopolar species whose interactions are dominated by the intermolecular dispersion energy. Eqn (4) is valid only for those mixtures where intermolecular forces are dominated by dispersion energy. In the original paper, Abe and Flory[3] have calculated the contact interaction parameter X_{12} from the excess molar enthalpy H_m^E data of corresponding mixtures, instead of using Eqn (4) and recommended this procedure. Hence, thereafter, it has been a common practice[48,49] to estimate X_{12} from H_m^E data of the corresponding mixture. One may refer to the recently published paper by Gepert *et al.*[47] for the correct method to evaluate X_{12}. Comparison of X_{12} (Table 4) derived from Eqn (4) and from H_m^E shows considerable discrepancies in the values of the two sets. Incorrect calculations of X_{12} may lead to both quantitative and qualitative differences in interpretation of molecular interactions. To visualise the sensitivity of P*, V* and X_{12}, more clearly, we compared excess internal pressure[50] π_{int}^E in Fig. 1, which demonstrates the effect of different approaches on the values of π_{int}^E.

Finally, the Eqns (2) and (3) are also dimensionally inconsistent, as it may be seen that the dimensions on the left and right hand sides are not same. It is apparent that the values of P* and V* reported in columns V and VI of Table 1 of ref 1 are of incorrect dimensions, V* should be $V^*/10^{-5}$ m^3 mol^{-1} and P* should be $P^*/10^2$ J cm^{-3} or $P^*/10^8$ J m^{-3}.

Conclusions

From the present analysis it is clear that the Ali–Tariq approach[1] to calculate thermal expansion coefficient α_p and isothermal compressibility κ_T for both organic liquids and liquid mixtures, using empirical relations (2) and (3) proposed by Pandey *et al.*[42] and claiming them to be the experimental values, is totally wrong, misleading and introduces errors in thermodynamic data. Eqns (2) and (3) are also dimensionally inconsistent. Flory's statistical theory should not have been applied to binary mixtures of polar components and with specific interactions. Finally, it is proper to emphasise here, once the correct expressions for calculating Flory's interaction parameter X_{12} are known, one should use only those expressions to derive X_{12} in the prediction of any thermodynamic property of liquid mixtures.

Table 3 APD between experimental α_P, κ_T, and π_{int} (Eqns 6 to 9) and those obtained using Eqns (1) to (3) for binary mixtures

Mix	T	APD		
	K	α_P	κ_T	π_{int}
DMSO + ethanol	298.15	13.7	14.2	3.5
Acetonitrile+ 1-hexanol	298.15	15.7	18.3	8.7
Acetonitrile+ DMF	303.15	20.8	10.6	12.2
Ethanol +1-octanol	303.15	26.0	22.5	4.7
Ethanol +1-hexanol	303.15	24.0	22.7	3.4
Benzene + 1-penol	308.15	15.8	15.4	5.3
Cyclohexane + 1-octanol	308.15	17.2	16.1	3.7
Cyclohexane + 1-decanol	308.15	20.6	16.8	4.9
THF+ 1-hexanol	308.15	15.0	12.6	3.8
THF+ 1-octanol	308.15	13.7	11.5	3.1
THF+ 1-decanol	308.15	14.8	11.5	3.6

Table 4 Flory's interaction parameter (X_{12}) from Eqn (4) and from H_m^E

mixtures	T	X_{12}		H_m^E
	K	from Eqn (4)	from H_m^E	Ref.
DMSO + ethanol	298.15	55.0	34.0	[31]
Acetonitrile + 1-hexanol	298.15	0.0	171.8	[11]
Acetonitrile + DMF	303.15	0.0	–25.5*	[12]*
Ethanol +1-octanol	303.15	24.5	14.1	[40]
Ethanol +1-hexanol	303.15	12.2	8.7	[40]
Benzene + 1-pentaol	308.15	9.6	34.6	[36]
Cyclohexane + 1-octanol	308.15	0.9	24.7	[37]
Cyclohexane + 1-decanol	308.15	3.4	22.7	[37]
THF+ 1-hexanol	308.15	1.4	53.2	[39]
THF+ 1-octanol	308.15	0.0	67.0	[39]
THF+ 1-decanol	308.15	1.5	60.1	[39]

*From equimolar V_m^E

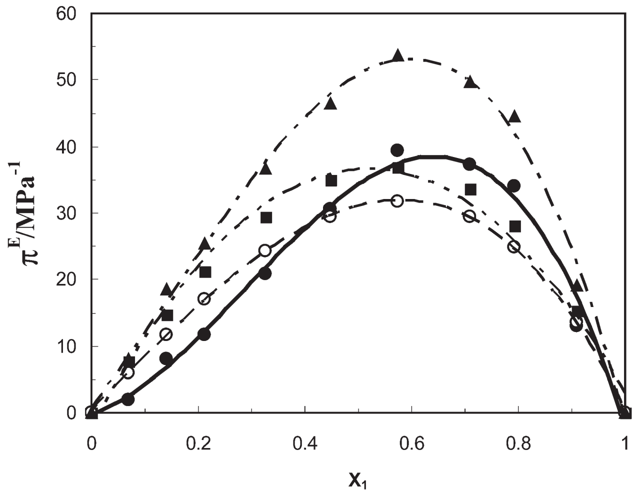

Fig. 1 Dependence of excess internal pressure on different approaches for DMSO–ethanol at 298.15 K. Experimental (●), Ali-Triq approach (▲), Flory theory with X_{12} from Eqn (4) (○) and Flory theory with X_{12} from H_m^E (■).

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