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

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Internal pressures of a number of binary liquid mixtures of varying natures of component liquids have been predicted using Flory's statistical theory. The predicted values have been compared with the experimentally calculated ones. Good approximation has been observed.

Keywords: internal pressure, liquid mixtures, Flory's statistical theory

The internal pressure, $\pi_i\left[=\left(\partial U/\partial V\right)_T\right]$ of a material is the volume derivative of the internal energy of the material at constant temperature. Its importance in the study of the thermodynamic properties of liquid mixtures was recognised by Hilderbrand.[1] Also, significant contributions were made by Barton,[2] Bagley *et al.*,[3] Rosseinsky,[4] Berkowitz *et al.*,[5] Renuncio *et al.*,[6] and Suryanarayana,[7] who have stressed that internal pressure is a fundamental property of the liquid state and correlated it with other thermodynamic parameters. Attempts have been made by some investigators[4,8,9] to calculate theoretically the internal pressure of liquids and their mixtures.

In recent years successful attempts have been made by Pandey and co-workers,[10-12] Patterson,[13] Heintz,[14] Bloomfield and Dewan,[15] Patterson and Delmas,[16] Aminabhavi *et al.*,[17] and Oswal and co-workers[18] to predict various useful thermodynamic and transport properties of liquid mixtures using Flory's statistical theory.[19-21] The success of Flory's theory for various liquid mixtures inspired us to propose an entirely new approach to calculate the internal pressure of binary liquid mixtures precisely. Except for the mole fraction, no other properties of liquid mixtures are needed for the present calculation. The results and method are reported in the present paper for computing the internal pressure of various binary liquid mixtures. The data needed for the present calculation were taken from our earlier works.[22-28]

Theory

The internal pressure of liquid mixtures can be experimentally calculated using the relation:[29]

$$\pi_{i(expt)}=\frac{\alpha T}{\beta_T} \qquad (1)$$

Experimental thermal expansivity, α_{expt}, and isothermal compressibility, $\beta_{T(expt)}$, can be calculated as:[30,31]

$$\alpha_{(expt)}=(0.0191\times\beta_T)^{1/4} \qquad (2)$$

$$\beta_{T(expt)}=\frac{1.71\times10^{-3}}{T^{4/9}u^{2}\rho^{4/3}} \qquad (3)$$

From Flory's theory isothermal compressibility, $\beta_{T(Flory)}$, for liquid mixtures can be given as:[32]

$$\beta_{T(Flory)}=\alpha T\tilde{V}^{2}/P^{*} \qquad (4)$$

Combining Eqns (4) and (1), we get,

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

Putting the values of characterstic pressure, P^* and reduced volume, $\tilde{V}$ for the mixtures using Flory's theory[21] compiled by Pandey *et al.*[12] in the above expression, one obtains the equation to compute the internal pressure of liquid mixtures using Flory's theory:[21]

$$\pi_{i(Flory)}=\frac{\left[\left(\sum_i\psi_iP_i^{*}\right)-\left(\sum_{i\neq j}\psi_i\theta_j\chi_{ij}\right)\right]}{\left(\tilde{v}^{o}+\tilde{v}^{E}\right)^{2}} \qquad (6)$$

The segment fraction, ψ_i, surface site fraction, θ_j, interaction parameter, χ_{ij}, ideal reduced volume, $\tilde{v}^{o}$, and excess reduced volume, $\tilde{v}^{E}$, for liquid mixtures can be computed by the methods described elsewhere.[12,21]

Table 1 Parameters for pure components

Components	Temp/K	$\alpha/10^3$ K^{-1}	$\beta_T/10^{11}$cm^2 dyn^{-1}	$V^*/10^5$ cm^3 mol^{-1}	$P^*/10^9$ Jcm^{-3}
Dimethylsulphoxide	298.15	1.010	5.452	5.707	8.623
Ethanol	298.15	1.281	14.116	4.501	4.590
	303.15	1.291	14.540	4.492	4.606
Acetonitrile	298.15	1.219	11.570	4.094	5.234
	303.15	1.228	11.910	4.095	5.251
Dimethylformamide	303.15	1.075	6.986	6.128	7.475
Tetrahydrofuran	308.15	1.191	10.520	6.358	5.829
Benzene	308.15	1.184	10.298	6.997	5.911
Trimethylpentane	308.15	1.407	20.530	12.61	3.756
Cyclohexane	308.15	1.257	13.067	8.431	5.052
1-Pentanol	308.15	1.219	11.549	8.445	5.480
1-Hexanol	298.15	1.288	10.446	9.751	5.598
	303.15	1.202	10.921	12.487	5.560
	308.15	1.203	10.967	9.758	5.670
1-Heptanol	308.15	1.191	10.516	11.07	5.829
1-Octanol	303.15	1.176	10.022	12.39	5.955
1-Decanol	308.15	1.163	9.580	14.99	6.199

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Table 2 Average percentage deviations (APD) of computed values using Flory's statistical theory compared with experimental values of internal pressure of liquid mixtures

Sample no.	Systems	Temperature/K	APD
1	DMSO + Ethanol	298.15	1.658
2	ACN + 1-Hexanol	298.15	1.795
3	ACN + DMF	303.15	1.286
4	Ethanol + 1-octanol	303.15	0.485
5	Ethanol + 1-hexanol	303.15	0.415
6	Benzene + 1-pentanol	308.15	1.585
7	Benzene + 1-heptanol	308.15	1.962
8	2,2,4 TMP + cyclohexane	308.15	0.464
9	Cyclohexane + 1-octanol	308.15	1.961
10	Cyclohexane + 1-decanol	308.15	1.507
11	THF + 1-hexanol	308.15	0.071
12	THF + 1-octanol	308.15	0.387
13	THF + 1-decanol	308.15	0.911

Equation (6) can be used to calculate the internal pressure of binary liquid mixtures using Flory's theory. The only data required for the present method are thermal expansivity, (α), isothermal compressibility, (β_T), and molar volume *(V)* of pure components and mole fraction of liquid mixtures.

Results and discussion

To test the accuracy of the presently proposed approach in predicting internal pressure of liquid mixtures, we have chosen 13 binary liquid systems of varying natures from our earlier works.[22-28] Using the reported ultrasonic speed, u, and density, ρ, data of liquid mixtures internal pressure have been calculated experimentally using Eqn (1). Internal pressure using Flory's statistical theory has been computed by putting the required parameters of pure components (Table 1) and reported mole fractions of the liquid mixtures in Eqn (6). The results are given (Table 2) in terms of average percentage deviation (APD) in experimentally calculated and theoretically computed values of internal pressure over the entire composition range of various mixtures. Nearly 150 data points were used for testing the present approach. APD values in the case of all the binary mixtures do not exceed 1.961 %. Another interesting observation is that the mixtures of two members of homologous series show relatively lower APD values as in case of systems 4, 5 (alkanol–alkanol) and system 8 (alkane–alkane) (Table 2). Thus, the results demonstrate the validity of the present approach. No further discussion is needed regarding the molecular interactions between the component molecules of the liquid mixtures as this has been discussed in our earlier communications.[22-28]

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