

Internal pressure, ultrasonic velocity and viscosity of multi-component liquid systems

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Abstract. Ultrasonic velocity, density and viscosity were measured in two ternary liquid systems namely, *n*-pentane + *n*-hexane + benzene (I) and *n*-hexane + cyclohexane + benzene (II) and one quaternary liquid system, *n*-pentane + *n*-hexane + benzene + toluene (III). The experimental as well as literature values of thermal expansion coefficient and iso-thermal compressibility of pure liquid components were utilized to deduce the ideal value of internal pressure and excess internal pressure for the above liquid systems at 298.15 K using two different approaches. In the conventional approach one needs the experimental values of α and β_T of mixtures for computing internal pressure, which was not possible. The second method which is proposed here utilizes only the density, ultrasonic velocity and viscosity data of the mixture. This method is used in computing internal pressure and its excess value for multicomponent liquid systems. A satisfactory agreement has been observed.

Keywords. Internal pressure; multicomponent liquid systems; ultrasonic velocity; density; viscosity; ternary liquid systems; quaternary liquid systems; excess internal pressure.

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1. Introduction

Internal pressure, a fundamental property of the liquid state has been studied initially by Hildebrand *et al* [1, 2] and subsequently by several workers [3–9]. For binary liquid mixtures, it has been used to investigate molecular interactions [6, 7, 10–12]. Due to lack of experimental data on thermal expansion coefficient (α) and isothermal compressibility (β_T) of liquid mixtures beyond binaries, the internal pressure could not be estimated for multicomponent systems. Direct experimentation of internal pressure through the thermal pressure coefficient for multicomponent liquid mixture has also not been done. The study of thermodynamic and transport properties of multicomponent liquid systems which has gained much importance during recent years [13] is dealt with in this work.

Suryanarayana [4] suggested an indirect method of evaluating internal pressure from the knowledge of viscosity, density and ultrasonic velocity. This approach has been extensively used for studying the internal pressure of pure liquids, binary liquid mixtures and solutions of electrolytes and non-electrolytes [12]. The proposed method for evaluating internal pressure has not been tested for various types of systems. This study extends this approach for estimating the internal pressure of ternary and quaternary liquid mixtures. To test its validity we have suggested an entirely different way to achieve the goal. For this, we have experimentally determined simultaneously the density, viscosity, and ultrasonic velocity of two ternary liquid systems namely:

n-pentane + *n*-hexane + benzene (I) and *n*-hexane + cyclohexane + benzene (II), and one quaternary liquid system i.e. *n*-pentane + *n*-hexane + benzene + toluene (III).

2. Theoretical

Thermodynamically, the internal pressure of a liquid, P_{int} is given by,

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

After some manipulation, the above expression at atmospheric pressure reduces to

$$P_{\text{int}} = \alpha T C_p M u^2 / \alpha^2 T V M u^2 + V C_p, \quad (2)$$

where u is the ultrasonic velocity and other symbols have their usual meaning. From this relation, the ideal value of P_{int} for multicomponent liquid system is obtained using the expression

$$(P_{\text{int}})_{\text{idl}} = \sum_{i=1}^n x_i (P_{\text{int}})_i, \quad (3)$$

where x_i is the mole fraction and $(P_{\text{int}})_i$ the internal pressure of the i th component in n -component liquid mixture.

In a series of papers, Suryanarayana *et al* [4] used an alternative method for computing the internal pressure of a liquid from its viscosity, density, and ultrasonic velocity. They obtained the following expressions for the internal pressure on the basis of dimensional analysis using free volume concept.

$$P_{\text{int}} = bRT \left(\frac{k\eta}{u} \right)^{1/2} \frac{\rho^{2/3}}{M^{7/6}}, \quad (4)$$

where b is packing factor, k is a constant independent of temperature having a value of 4.28×10^9 and η is the viscosity. The other symbols have their usual meaning. Thus (4) affords a method for estimating P_{int} from a knowledge of η , ρ , and u and does not require the values of α and β_T . For liquid mixtures, (4) can be written as

$$(P_{\text{int}})_{\text{mix}} = bRT \left(\frac{k\eta_{\text{mix}}}{u_{\text{mix}}} \right)^{1/2} \frac{\rho_{\text{mix}}^{2/3}}{M_{\text{mix}}^{7/6}}. \quad (5)$$

M_{mix} is given by

$$M_{\text{mix}} = \sum_{i=1}^n x_i M_i, \quad (6)$$

whereas (1) can be written as (at $P = 0$)

$$(P_{\text{int}})_{\text{mix}} = \frac{\alpha_{\text{mix}} T}{(\beta_T)_{\text{mix}}}. \quad (7)$$

The excess internal pressure (P_{int}^E), of n -component liquid mixture is given by

$$P_{\text{int}}^E = (P_{\text{int}}^E)_{\text{mix}} - \sum_{i=1}^n x_i (P_{\text{int}})_i \quad (8)$$

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$(P_{\text{int}})_{\text{mix}}$ is the internal pressure of the mixture that includes all types of interactions. In a multicomponent system having $n = 3$ or 4 , for each of the pure component, i , (1) and (4) can be expressed as (at $P = 0$)

$$(P_{\text{int}})_i = \frac{\alpha_i T}{(\beta_T)_i}, \quad (9)$$

$$(P_{\text{int}})_i = bRT \left(\frac{K\eta_i}{u_i} \right)^{1/2} \frac{\rho_i^{2/3}}{M_i^{7/6}}. \quad (10)$$

3. Experimental

All the organic liquids used were of Analar grade and were obtained from BDH Chemicals, England. These chemicals were further purified. Densities, viscosities, and ultrasonic velocities were measured at 298.15 K. Densities were determined with a bicapillary pycnometer with an accuracy of $\pm 0.3 \text{ kg/m}^3$ (approx. 0.05%). Ultrasonic velocity measurements were made using a crystal controlled variable path ultrasonic interferometer with an accuracy of 5.7 ms^{-1} . Viscosities were measured using pre-calibrated Ubbelohde type of viscometer. Viscosity measurement is based on the measurements of time in which a constant volume of liquid flows through a capillary with an accuracy of $\pm 0.54\%$. Density and ultrasonic velocity of quaternary liquid system n -pentane + n -hexane + benzene + toluene have been reported in a recent paper [14].

4. Results and discussion

The two ternary liquid mixtures and one quaternary liquid mixture taken for the present investigations are: n -pentane + n -hexane + benzene (I), n -hexane + cyclohexane + benzene (II), and n -pentane + n -hexane + benzene + toluene (III). Density, ultrasonic velocity, viscosity and other thermodynamic parameters e.g. thermal expansion coefficient (α) and iso-thermal compressibility (β_T) of pure component liquids are recorded in table 1. Experimentally determined values of η , u , and ρ for various ternary liquid systems at 298.15 K are reported in tables 2–4.

Internal pressure values for all the pure component liquid systems (I)–(III) were calculated from (1) and (4) and are given in columns six and seven of table 1. Literature values of thermal expansion coefficient (α) and iso-thermal compressibility (β_T) are given in columns four and five respectively of table 1. Experimentally measured values of density (ρ), ultrasonic velocity (u), and viscosity (η) of I, II and III at 298.15 K as functions of mole fractions of various components are presented in columns three, four and five respectively of tables 2 and 3 and columns four, five and six respectively of table 4. From the internal pressure of pure component liquids, the internal pressure of the ideal mixture is calculated using (3). Thus, we obtain two sets of $(P_{\text{int}})_{\text{idl}}$ values; one from (3) and (9) and the other from (3) and (10) respectively. These values are recorded in columns six and seven of tables 2 and 3 respectively. However, in table 4, these values are listed in columns seven and eight respectively. Due to the lack of experimental data of α and β_T for the multicomponent liquid systems, only (5) has been used to obtain $(P_{\text{int}})_{\text{mix}}$ using the presently determined values of ρ , u , and η . Column eight of tables 2 and 3 and column nine of table 4 enlists the values of $(P_{\text{int}})_{\text{mix}}$ for the respective liquid systems. From the values of $(P_{\text{int}})_{\text{mix}}$ and $(P_{\text{int}})_{\text{idl}}$,

Table 1. Density (ρ), ultrasonic velocity (u), viscosity (η), and other thermodynamic parameters for pure component liquids at 298.15 K.

Liquids	$\rho \times 10^{-3}$ (kg m ⁻³)	u (ms ⁻¹)	$\eta \times 10^3$ (NS m ⁻²)	$\alpha \times 10^{13}$ * (k ⁻¹)	$\beta_r \times 10^{12}$ * (m ² N ⁻¹)	P_{int} (atm)	
						Eq. (1)	Eq. (4)
Benzene	0.8732	1296.0	0.5961	1.2265	96.70	3732	3886
Cyclohexane	0.7734	1252.0	0.8950	1.2150	114.00	3136	4092
n-Hexane	0.6552	1076.6	0.2940	1.3897	160.60	2546	2203
Toluene	0.8627	1304.0	0.6036	1.0740	92.15	3432	3186
n-Pentane	0.6216	990.0	0.2166	1.6225	212.30	2249	2340

* [15, 16]

Table 2. Density, ultrasonic velocity, viscosity, internal pressure and excess internal pressure for system (I): n-Pentane (x_1) + n-hexane(x_2) + benzene(x_3) at 298.15 K.

x_1	x_2	$\rho \times 10^{-3}$ (kg m ⁻³)	u (ms ⁻¹)	$\eta \times 10^3$ (NSm ⁻²)	$(P_{i,int})$ (atm) Eqs (3) & (9)	$(P_{i,int})$ (atm) Eqs (3) & (10)	$(P_{i,mix})$ (atm) Eq. (5)	P_{i}^E atm Eq. (8)	$\Delta(P_{i,int})$
0.0966	0.0471	0.7432	1201.2	0.3863	3094	3035	2800	-235	-1.94
0.1428	0.3739	0.7416	1197.5	0.3802	3077	3036	2803	-233	-1.35
0.2017	0.3383	0.7361	1193.2	0.3723	3032	3005	2790	-215	-0.90
0.2590	0.3038	0.7286	1187.7	0.3553	2988	2975	2739	-236	-0.44
0.2984	0.2877	0.7218	1177.2	0.3297	2948	2941	2647	-294	-0.24
0.3075	0.2945	0.7175	1175.2	0.3253	2927	2915	2622	-293	-0.41
0.3420	0.3143	0.7073	1173.4	0.3221	2852	2829	2587	-242	-0.81
0.3685	0.3523	0.6953	1170.2	0.3098	2768	2724	2507	-217	-1.62
0.4099	0.3888	0.6838	1178.4	0.3199	2663	2598	2509	-89	-2.50
0.4082	0.4665	0.6688	1163.2	0.3001	2574	2470	2387	-83	-4.21

Table 3. Density, ultrasonic velocity, viscosity, internal pressure and excess internal pressure for system (II): *n*-hexane (x_1) + cyclohexane(x_2) + benzene(x_3) at 298.15 K.

x_1	x_2	$\rho \times 10^{-3}$ (kg m^{-3})	u (ms^{-1})	$\eta \times 10^3$ (Nsm^{-2})	$(P_i)_{\text{int}}(\text{atm})$ Eqs (3) & (9)	$(P_i)_{\text{int}}(\text{atm})$ Eqs(3) & (10)	$(P_i)_{\text{mix}}(\text{atm})$ Eq. (5)	$P_i^E(\text{atm})$ Eq. (8)	$\Delta(P_i)_{\text{int}}$
0.0771	0.4315	0.8062	1278.1	0.6253	3384	3845	3622	-223	11.99
0.1269	0.4149	0.7935	1267.5	0.5923	3334	3758	3488	-270	11.28
0.1795	0.3854	0.7852	1261.2	0.5889	3290	3664	3449	-215	10.21
0.2279	0.3501	0.7770	1251.2	0.5595	3253	3575	3344	-231	9.01
0.2616	0.3342	0.7733	1263.5	0.5632	3223	3515	3320	-195	8.31
0.2812	0.3348	0.7672	1256.3	0.5239	3199	3482	3187	-295	8.13
0.3021	0.3643	0.7618	1260.2	0.5521	3157	3453	3235	-218	8.57
0.3062	0.3823	0.7585	1248.4	0.5423	3141	3450	3205	-245	8.96
0.3448	0.4566	0.7480	1259.1	0.5608	3051	3400	3182	-218	10.26
0.3231	0.4851	0.7481	1244.2	0.5598	3060	3442	3198	-244	11.10

Table 4. Density, ultrasonic velocity, viscosity, internal pressure and excess internal pressure for system (III): (*n*-pentane (x_1) + *n*-hexane (x_2) + benzene (x_3) + toluene (x_4)) at 298.15 K.

x_1	x_2	x_3	$\rho \times 10^{-3}$ (kg m^{-3})	μ (ms^{-1})	$\eta \times 10^3$ (NSm^{-2})	$(P_{\text{int}})_{\text{dil}}$ (atm) Eqs (3) & (9)	$(P_{\text{int}})_{\text{dil}}$ (atm) Eqs (3) & (10)	$(P_{\text{int}})_{\text{mix}}$ (atm) Eq. (5)	P^E (atm) Eq. (8)	$\Delta(P_i)_{\text{dil}}$
0.0943	0.0918	0.4587	0.8216	1260.1	0.4692	3377	3337	3113	-224	-1.19
0.1300	0.1373	0.2974	0.8011	1233.2	0.4283	3246	3150	2905	-245	-3.05
0.1278	0.1288	0.3589	0.8054	1237.3	0.4515	3274	3203	3020	-183	-2.22
0.1450	0.1291	0.3376	0.7991	1225.7	0.4431	3247	3173	2992	-181	-2.33
0.1492	0.1384	0.3421	0.7974	1217.9	0.4102	3235	3164	2902	-262	-2.24
0.1843	0.1484	0.2711	0.7855	1200.1	0.4050	3164	3074	2856	-218	-2.93
0.1823	0.1640	0.3613	0.7838	1197.9	0.3912	3179	3124	2856	-268	-1.76
0.1819	0.1606	0.3842	0.7824	1200.1	0.3992	3190	3143	2745	-398	-1.49
0.1250	0.1665	0.2455	0.7975	1223.1	0.4123	3210	3089	2827	-262	-3.92
0.1691	0.2041	0.2218	0.7769	1201.3	0.3810	3118	2998	2637	-361	-4.00
0.1866	0.0826	0.1250	0.7995	1229.3	0.3893	3175	3035	2710	-325	-4.61
0.1372	0.1580	0.5548	0.7926	1211.4	0.4035	3296	3303	2983	-320	+0.21
0.0660	0.1053	0.7033	0.8273	1268.1	0.4598	3472	3519	3219	-300	+1.33
0.0524	0.1434	0.4201	0.8176	1260.5	0.4493	3369	3295	2991	-304	-2.24
0.1568	0.0468	0.4582	0.8184	1256.3	0.4223	3342	3328	2991	-337	-0.42

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the excess internal pressure, (P_{int}^E) was calculated using (8) and these values are recorded in column nine of tables 2 and 3 and column ten of table 4. Thus, in the present study we have succeeded in estimating the excess internal pressure of all the systems from the viscosity, density, and ultrasonic velocity data. The last column of tables 2–4, records the percentage deviations between the ideal internal pressure values, (P_{int}^E)_{idl}, obtained from (3) and (9) and those from (3) and (10).

A perusal of tables 2–4, shows that the ideal values of internal pressure (P_{int}^E)_{idl}, calculated from both the methods are in good agreement for all the systems investigated with a maximum deviation of 12%. Small deviations between the two sets of values may be attributed to the uncertainties in the experimental data of α , β_T , ρ , u , and η . In some cases the percentage deviations are even less than one per cent. Hence, we conclude that Suryanarayana [4] approach for estimating internal pressure of multicomponent liquid mixtures, based on dimensional analysis using thermodynamic considerations is very well applicable. This permits the determinations of internal pressure of multicomponent liquid systems purely from density, ultrasonic velocity and viscosity data. As far as we know, the experimental values of α and β_T are not available for multicomponent liquid systems. Moreover, both these parameters are very sensitive and need quite an accurate method for determination.

The values of excess internal pressure (P_{int}^E), obtained from viscosity, density, and ultrasonic velocity data for all the systems appear to be functions of mole fractions of all the liquid components present in the mixture. This confirms our earlier findings on binary liquid mixtures [9, 10]. Thus we express

$$P_{\text{int}}^E = f(x_1, x_2, x_3, x_4, \dots).$$

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