

Theoretical evaluation of internal pressure in ternary and sub-binary liquid mixtures at various temperatures

J. Madhumitha, N. Santhi*, G. Alamelumangai, M. Emayavaramban

Department of Chemistry, Government Arts College, C.Mutlur, Chidambaram – 608102, India

*E-mail address: nsaanthi@gmail.com

ABSTRACT

The Internal pressures of Ternary and their sub-Binary liquid mixtures of benzene(1) + hexane(2) + sec-butyl alcohol(3) were calculated using density, velocity and molar refraction from the temperature range of 303.15K-318.15K. For the Binary liquid mixtures, the Experimental Internal pressure values were correlated through an equation proposed by Andiappan et.al. For the Ternary liquid mixture, the Experimental Internal pressure values were correlated through an equation proposed by us. The Experimental values and the Theoretical values are in close agreement with each other.

Keywords:

Ternary liquid mixtures, sub-binary liquid mixtures, benzene, hexane, sec-butyl alcohol

1. INTRODUCTION

The Internal pressure is the cohesive force, which is a resultant of forces of attraction and forces of repulsion between molecules in a liquid, and considerable importance can be gained by simply observing and comparing internal pressure-volume curves for pure liquids¹. The term a/v^2 in Vander waals² equation being the measure of attractive force of the molecule is called the cohesive or internal pressure. The intermolecular forces give a liquid its cohesion and it creates a pressure of thousand to ten thousands atmospheres within a liquid. Cohesion creates a pressure within a liquid of between 10^3 to 10^4 atmospheres. The internal pressure thus depends markedly on the molar volume, and also on the external pressure. It should be emphasized that the internal pressure is also sensitive to the repulsive component in a liquid³.

Non-polar liquids have low internal pressures of the order of 2000 to 3000 atm; polar liquids have somewhat larger values, hydrogen bonding still increasing the value, water having a value around twenty thousand atmospheres^{3,4}. The importance of internal

pressure in understanding the properties of liquids and the full potential of internal pressure as a structural probe did become apparent with the Pioneering work of Hildebrand^{5,6}. In an excellent article Dack⁷ reviewed the importance of solvent internal pressure and cohesion to solution phenomena. The internal pressure is a single factor which varies due to all type of solvent-solute, solute-solute and solvent-solvent interactions. The Various thermodynamic properties and molecular interactions involving self-associated alcohols and phenols helps in understanding the inter and intramolecular interactions.

Stavely et al⁸ compared the internal pressure of individual liquid components and predicted the interaction in liquid mixtures. Richards⁹ pointed out the importance of internal pressure in understanding the physical properties of liquids and solids. An extensive list of values of internal pressure for liquids has been given by Allen et al¹⁰.

2. MATERIALS AND METHODS

The chemicals used in the present work are Analar grade and purified by the standard methods¹¹. The purity of samples are checked out by measuring their density, boiling point and refractive index (Table 1.).

Table 1. The Physical constants of pure liquids are given in the following table.

Liquid	Density(g/cm ³)		Boiling point		Refractive Index(n)	
	303.15K	298K	(°C)		303.15K	308.15K
-----	Exp	Lit ¹²	Exp	Lit ¹²	Exp	Lit ¹²
n-hexane	0.6493	0.6548	68.70	68.74	1.496	1.493
Benzene	0.8675	0.8736	80.10	80.103	1.372	1.37
sec-butyl alcohol	0.7988	0.8026	99.50	99.52	1.393	1.391

Ultrasonic velocities of pure liquids and liquid mixtures from the temperature range of 308K to 318K were measured using Ultrasonic Interferometer operating at 3 MHz. The density was determined at the experimental temperatures using 10 ml capacity specific gravity bottle immersed in a thermostatic bath (accuracy +0.01 °C). The volume of the bottle at the experimental temperature, viz. 308K-318K was ascertained using doubly distilled water.

3. THEORY AND CALCULATION

Srivastava and Berkowitz Equation¹² equation was used to compute internal pressure from the measurement of ultrasonic velocity, density and refractive index.

Srivastava and Berkowitz Equation is

$$U \sqrt{D} = K' \sqrt{(Rm)\pi_i} \quad (1)$$

Where:

U = Ultrasonic velocity

D = Density

Rm = Molar refraction

K' = distinctly structure dependent Constant

π_i = Internal pressure

If the data for ultrasonic velocity, density, Molar refraction, internal pressure of pure liquids are known, the constant (K') can be determined using equation (1).

Srivastava and Berkowitz Equation for the Binary Liquid Mixtures is

$$(\pi_i)_{12} = \frac{U_{12} \sqrt{D_{12}}}{(x_1 K'_1 + x_2 K'_2) \sqrt{(Rm)_{12}}} \quad (2)$$

Where

U_{12} = Ultrasonic velocity of the binary mixture

D_{12} = Density of the binary mixture

$(Rm)_{12}$ = Molar refraction of the binary mixture

x_1 and x_2 are Mole fractions of components (1) and (2)

K'_1 and K'_2 are distinctly structure dependent constants

$(\pi_i)_{12}$ = Internal pressure of the binary mixture

Evaluation of Rm:

$$Rm = \left(\frac{n^2 - 1}{n^2 + 2} \right) \left(\frac{x_1 m_1 + x_2 m_2}{d} \right) \quad (3)$$

Where

n = refractive index

x₁ and x₂ are Mole fractions of components (1) and (2)

m₁ and m₂ are Molecular weight of components (1) and (2)

d = density

The Andiappan et al¹³ equation was used to calculate the theoretical internal pressure of binary liquid mixtures.

Andiappan et al equation is

$$\log \pi_i = x_1 \log \pi_1 + x_2 \log \pi_2 - \beta x_1 x_2 \quad (4)$$

Where x₁ and π₁ are the mole fraction and internal pressure of the component 1 and x₂ and π₂ are the mole fraction and internal pressure of the component 2. The equation (4) containing only one constant β, has been employed for correlating the experimental data.

The experimentally determined internal pressure data for all the three binary systems have been correlated through equation (4) at temperatures 303.15K to 318.15K (Table 3). Constant β has been determined through a least square method at all the temperatures.

Srivastava and Berkowitz equation for the Ternary liquid mixture is written as

$$(\pi_i)_{123} = \frac{U_{123} \sqrt{D_{123}}}{(x_1 K_1' + x_2 K_2' + x_3 K_3') \sqrt{(Rm)_{123}}} \quad (5)$$

Where

U₁₂₃ = Ultrasonic velocity of the ternary mixture

D₁₂₃ = Density of the ternary mixture

(Rm)₁₂₃ = Molar refraction of the ternary mixture

x₁, x₂ and x₃ are Mole fractions of components (1), (2) and (3)

K₁', K₂' and K₃' are distinctly structure dependent constants

(π_i)₁₂₃ = Internal pressure of the ternary mixture

In the present work, the equation (4) for ternary system is modified as

$$\log \pi_i = x_1 \log \pi_1 + x_2 \log \pi_2 + x_3 \log \pi_3 + x_1 x_2 (\beta_{12} (x_1 - x_2)) + x_2 x_3 (\beta_{23} (x_2 - x_3)) + x_3 x_1 (\beta_{31} (x_3 - x_1)) - C x_1 x_2 x_3 \quad (6)$$

Where

β_{12} = binary interaction constant for 1, 2 component

β_{23} = binary interaction constant for 2, 3 component

β_{31} = binary interaction constant for 3, 1 component

The constants β_{12} , β_{23} and β_{31} are determined from equation (4) using least square method. Constant C has been determined through a least square method at all the temperatures.

4. RESULTS AND DISCUSSION

For the Ternary and sub-binary systems, the internal pressure values are evaluated from the temperature range of 303.15K to 318.15K. These values are correlated through equations (4) and (6) is shown in Tables (2 & 3).

Table 2. Experimental and Calculated Internal pressures(in atm)

System benzene(1) + hexane(2)								
Mol Frac	303.15K		308.15K		313.15K		318.15K	
	EXP	CAL	EXP	CAL	EXP	CAL	EXP	CAL
x1								
0.1016	2236.0	2225.2	2172.1	2166.3	2125.2	2115.0	2085.4	2073.9
0.201	2300.0	2289.4	2236.5	2227.3	2184.0	2174.1	2141.1	2130.5
0.301	2371.6	2363.7	2304.8	2298.5	2249.1	2243.2	2201.8	2197.0
0.4008	2449.0	2448.3	2377.8	2380.0	2322.2	2322.6	2274.4	2273.9
0.5017	2529.8	2545.3	2462.7	2474.1	2401.4	2414.5	2351.2	2363.1
0.6014	2645.2	2653.7	2575.0	2579.8	2511.5	2517.8	2456.5	2463.8
0.7033	2778.5	2778.6	2703.8	2702.1	2639.4	2637.7	2580.4	2580.9

0.7993	2914.4	2910.8	2834.5	2832.1	2764.4	2765.3	2705.0	2705.8
0.8998	3070.8	3065.8	2987.8	2985.2	2921.8	2915.7	2861.0	2853.5
	$\beta = 0.0715$		$\beta = 0.0759$		$\beta = 0.0777$		$\beta = 0.0801$	
	ABSD = 0.2821%		ABSD = 0.2136%		ABSD = 0.2574%		ABSD = 0.2676%	
System sec-butyl alcohol(1) + hexane(2)								
Mol Frac	303.15K		308.15K		313.15K		318.15K	
x1	EXP	CAL	EXP	CAL	EXP	CAL	EXP	CAL
0.1051	2251.821	2242.171	2197.044	2186.876	2148.036	2137.765	2106.187	2097.732
0.2041	2336.198	2321.357	2280.573	2265.915	2231.305	2216.765	2188.25	2175.055
0.3141	2432.489	2421.634	2377.999	2365.713	2329.011	2316.144	2284.128	2272.242
0.4023	2509.541	2512.268	2452.494	2455.71	2402.837	2405.494	2359.853	2359.556
0.5058	2619.412	2631.409	2563.365	2573.794	2512.983	2522.431	2464.492	2473.753
0.5999	2741.206	2752.911	2680.968	2694.021	2626.262	2641.214	2574.64	2589.677
0.6989	2891.067	2895.762	2828.863	2835.172	2773.274	2780.385	2717.814	2725.412
0.8222	3099.669	3097.818	3034.703	3034.54	2976.773	2976.53	2917.002	2916.578
0.9004	3251.553	3241.483	3188.756	3176.129	3129.086	3115.579	3065.171	3052.011
	$\beta = 0.0284$		$\beta = 0.0281$		$\beta = 0.0285$		$\beta = 0.0294$	
	ABSD = 0.1949%		ABSD = 0.1884%		ABSD = 0.1773%		ABSD = 0.1895%	
System sec-butyl alcohol(1) + benzene(2)								
Mol Frac	303.15K		308.15K		313.15K		318.15K	
x1	EXP	CAL	EXP	CAL	EXP	CAL	EXP	CAL
0.1013	3276.863	3263.685	3203.142	3190.139	3135.071	3121.772	3075.374	3062.657
0.2018	3275.251	3270.697	3203.308	3198.188	3136.963	3130.87	3079.084	3070.76
0.3029	3286.307	3282.14	3212.884	3210.547	3146.972	3144.261	3086.241	3083.196

0.4024	3294.1	3297.746	3222.938	3226.929	3158.048	3161.64	3096.574	3099.683
0.5045	3304.602	3318.304	3235.83	3248.156	3173.001	3183.878	3110.972	3121.052
0.5998	3337.368	3341.721	3268.732	3272.083	3204.457	3208.741	3138.352	3145.146
0.7001	3383.79	3370.869	3312.863	3301.65	3248.332	3239.292	3182.214	3174.931
0.8011	3404.81	3405.006	3337.484	3336.088	3274.23	3274.723	3210.39	3209.639
0.8981	3440.941	3442.441	3371.347	3373.697	3313.57	3313.295	3248.548	3247.561
	$\beta = 0.0284$		$\beta = 0.0281$		$\beta = 0.0285$		$\beta = 0.0294$	
	ABSD = 0.1949%		ABSD = 0.1884%		ABSD = 0.1773%		ABSD = 0.1895%	

Table 3. Experimental and Calculated Internal pressures(in atm) for the system benzene(1) + hexane(2) + sec-butyl alcohol(3)

Experimental and Calculated Internal pressures(in atm) for the system benzene(1) + hexane(2) + sec-butyl alcohol(3)									
Mol Frac		303.15K		308.15K		313.15K		318.15K	
x1	x2	EXP	CAL	EXP	CAL	EXP	CAL	EXP	CAL
0.1225	0.7894	2318.604	2372.167	2278.551	2317.373	2226.607	2267.348	2180.408	2226.415
0.2202	0.6873	2375.289	2440.105	2326.719	2387.119	2279.219	2337.243	2231.527	2295.946
0.3708	0.5247	2493.667	2548.28	2441.336	2496.091	2392.881	2445.825	2340.945	2403.063
0.4008	0.4967	2562.317	2571.26	2510.251	2518.581	2460.889	2467.873	2408.214	2424.626
0.4991	0.3992	2656.839	2674.647	2601.583	2620.553	2541.165	2568.28	2499.886	2523.352
0.6004	0.3002	2765.77	2814.948	2714.587	2758.523	2661.907	2703.879	2606.436	2656.798
0.6822	0.2354	2865.034	2927.488	2807.375	2867.366	2753.643	2809.668	2701.495	2760.357
0.7855	0.1322	3045.295	3086.881	2988.739	3021.499	2938.266	2960.151	2882.8	2907.386
0.1295	0.6904	2400.224	2440.035	2352.114	2386.885	2304.89	2338.778	2253.494	2296.96
0.2007	0.5985	2472.312	2481.023	2391.404	2431.291	2341.318	2384.726	2296.4	2343.179
0.2822	0.4966	2536.275	2533.49	2480.521	2486.263	2427.991	2440.84	2378.685	2399.095
0.4225	0.356	2644.701	2653.66	2596.796	2605.957	2546.943	2559.466	2496.079	2515.948

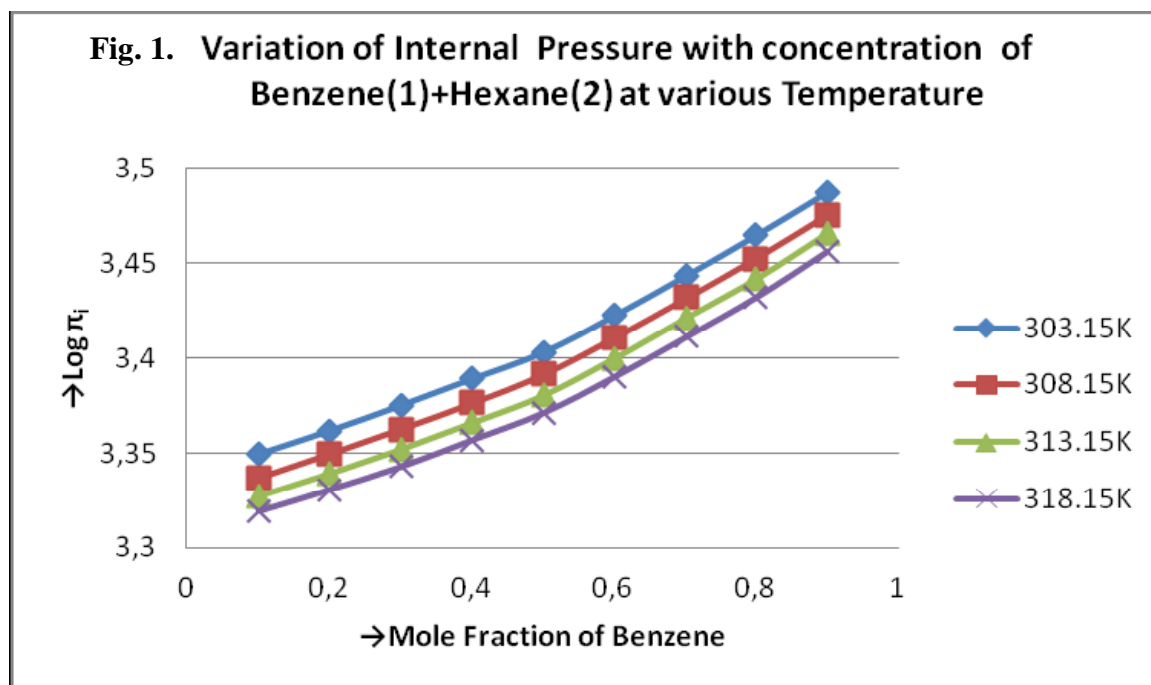
0.5212	0.2586	2771.755	2795.807	2718.175	2745.123	2670.034	2696.231	2609.653	2650.302
0.6061	0.1946	2882.3	2916.638	2832.512	2861.363	2786.356	2809.038	2731.935	2760.555
0.6766	0.1357	3039.526	3034.114	2987.92	2973.576	2926.137	2917.794	2879.654	2866.487
0.1205	0.5897	2513.491	2521.662	2458.413	2468.686	2411.655	2422.619	2365.829	2379.263
0.1999	0.4964	2569.775	2551.949	2528.281	2503.561	2476.672	2459.563	2441.955	2416.95
0.3215	0.3581	2669.675	2637.039	2614.556	2590.839	2557.943	2547.625	2509.907	2504.179
0.4218	0.257	2748.04	2770.923	2697.731	2722.382	2646.064	2677.179	2597.626	2631.461
0.4948	0.1917	2886.244	2887.913	2836.98	2835.369	2787.968	2787.437	2732.19	2739.264
0.5898	0.1203	3048.861	3040.701	2994.359	2980.958	3153.783	2928.345	2889.499	2876.473
0.1225	0.4927	2580.154	2606.145	2529.185	2552.861	2452.47	2508.629	2426.088	2463.65
0.2016	0.3763	2698.176	2673.83	2647.801	2624.081	2596.45	2581.822	2539.909	2536.684
0.3243	0.2543	2805.155	2792.252	2760.872	2742.343	2709.862	2699.014	2659.636	2652.11
0.4215	0.1764	2905.422	2915.624	2873.824	2861.956	2814.718	2815.688	2765.614	2766.188
0.4839	0.1156	3067.454	3044.866	3013.547	2985.109	2960.688	2935.52	2910.56	2882.718
0.1272	0.3973	2715.183	2715.181	2661.703	2660.105	2609.531	2616.79	2538.549	2569.456
0.2002	0.3186	2803.156	2763.374	2749.243	2711.049	2713.088	2668.554	2661.224	2621.245
0.2984	0.2205	2934.301	2869.548	2879.298	2816.384	2825.372	2772.81	3024.923	2723.775
0.3973	0.1128	3100.427	3069.24	3028.384	3007.933	2991.066	2960.133	2923.14	2906.1
0.1275	0.3	2893.766	2870.817	2808.343	2811.121	2756.968	2767.328	2695.534	2716.176
0.2	0.2187	2961.039	2943.526	2904.304	2884.664	2857.306	2841.071	2801.644	2789.106
0.3039	0.1155	3117.227	3103.552	3065.126	3039.731	3003.369	2993.429	2944.565	2937.968
0.1116	0.2182	3102.194	3036.133	3038.374	2969.591	2975.374	2924.819	2916.132	2869.075
0.1801	0.1396	3147.3	3126.911	3083.545	3059.496	3055.883	3014.475	3021.898	2957.275
		C = 1.0370		C = 0.9539		C = 0.9207		C = 0.8938	
		ABSD = 0.9816%		ABSD = 1.0060%		ABSD = 1.1969%		ABSD = 1.3752%	

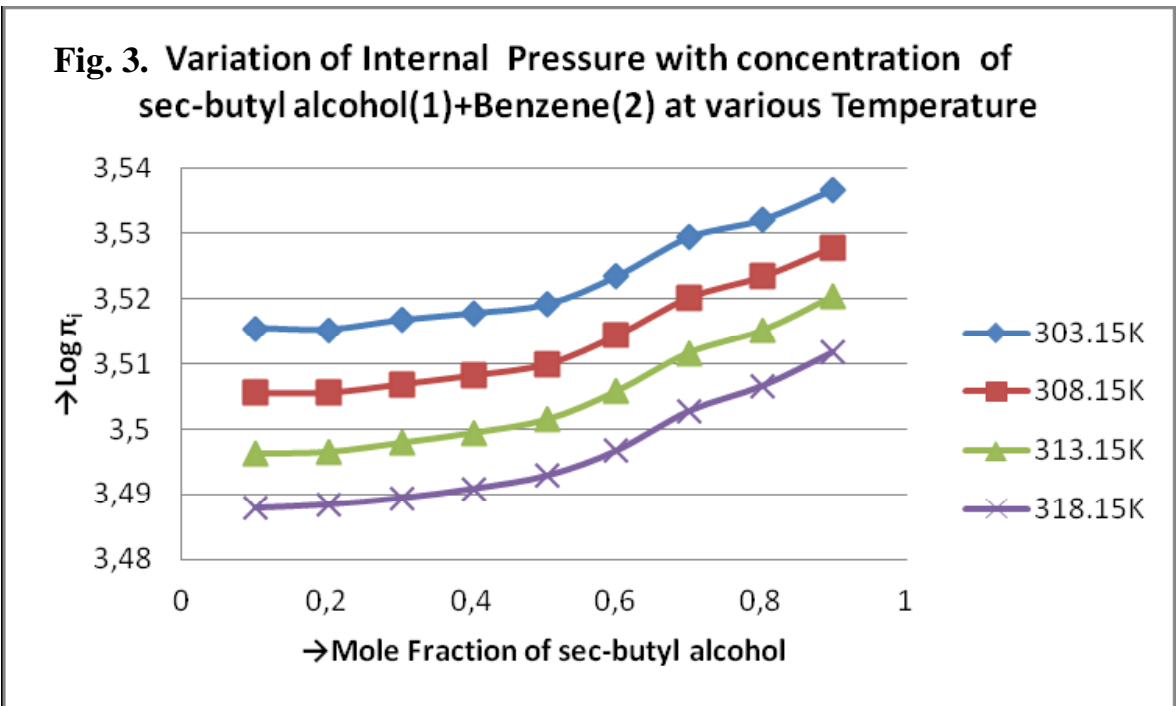
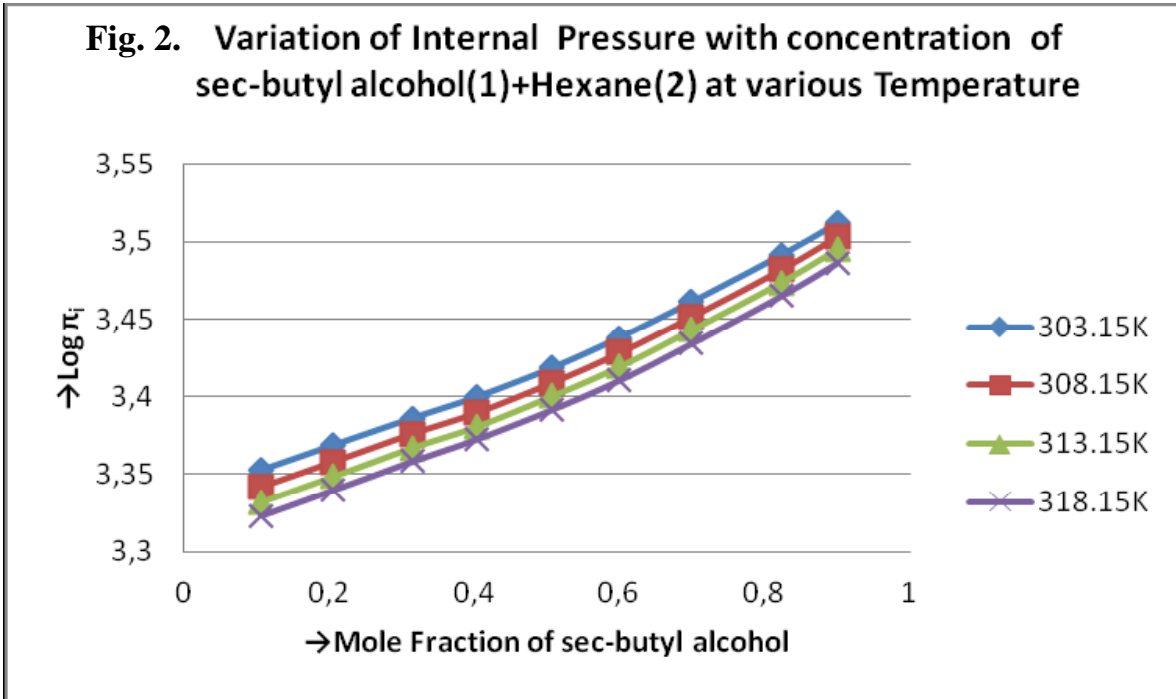
Both the Experimental and Theoretical Internal pressure values are represented in the tables (2 & 3). It is known from the tables that both the experimental and the theoretical internal pressure values are more comparable with each other. By using least square method, the Interaction constants (β) and (C) are evaluated from the temperature range of 303.15K to 318.15K. The absolute average deviation between the experimental and correlated Internal Pressure values for all the binary systems varies from 0.17% to 0.38%. The Interaction constant (β) evaluated for all the binary systems varies from 0.02 to 0.08.

It is known from the tables (2) & (3) that the increase in internal pressure values with increase of alcohol concentration is probably due to Hydrogen bonding. Since alcohols are strongly self-associated liquid having a three dimensional network of Hydrogen bond¹⁴. So it is apparent that when two interacting molecules are having some sort of attractive forces like that of hydrogen bonding should result in increase of internal pressure¹⁵. The hydrogen bonding arises from short range interaction augmented by the fact that Hydrogen bond distance (A-H--B) is greater than Vander Waals radii. The short range forces arise when the molecules come close enough together causing a significant overlap of electron clouds and are often highly directional¹⁶.

The non-linear relationship is more obvious for sec-butyl alcohol and benzene. This may be due to the interaction of the delocalized π -bond electron cloud with the sec-butyl alcohol. Benzene is a non-polar and an inert aromatic solvent. The dissociation effect of benzene molecule prevents self-association in associated alcohol molecules. The π -electron cloud of benzene is responsible for the dissociation effect.

The Internal pressure varies with respect to the concentration and Temperature. This is shown in graph. Figures 1-3 shows a linear variation of internal pressure with the concentration for binary liquid mixtures from the temperature range of 303.15K to 318.15K.



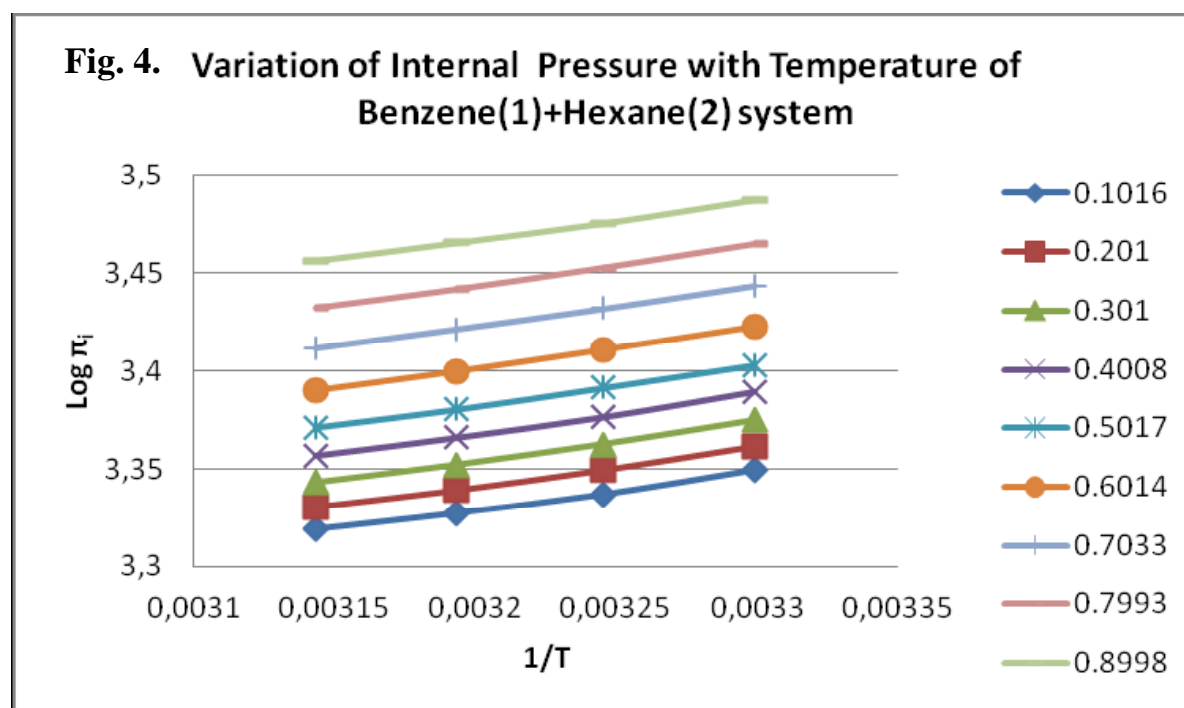


From the Tables 2 & 3 it is known that the decrease in internal pressure values with increase of temperature is due to the decrease in cohesive forces. The reduction in internal pressure may be due to the loosening of cohesive forces leading to breaking the structure of the solute.

When the temperature is increased, there is a tendency for the solute molecules to move away from each other, reducing the possibility for the interaction, which may further reduce the cohesive forces¹⁷. Due to weakening of intermolecular forces of attraction the internal pressure should fall. This is an important observation which we have made and which is to be expected theoretically also as cohesive forces between molecules becoming less with increasing temperature¹⁸.

Figures (4-6) shows a linear variation of internal pressure with the reciprocal of temperature for binary liquid mixtures from the temperature range of 303.15K-313.15K. The absolute average deviation between the experimental and correlated values for the Ternary system varies from 0.98% to 1.37%.

The evaluated Interaction constant (C) for the Ternary system varies from 0.89 to 1.03.

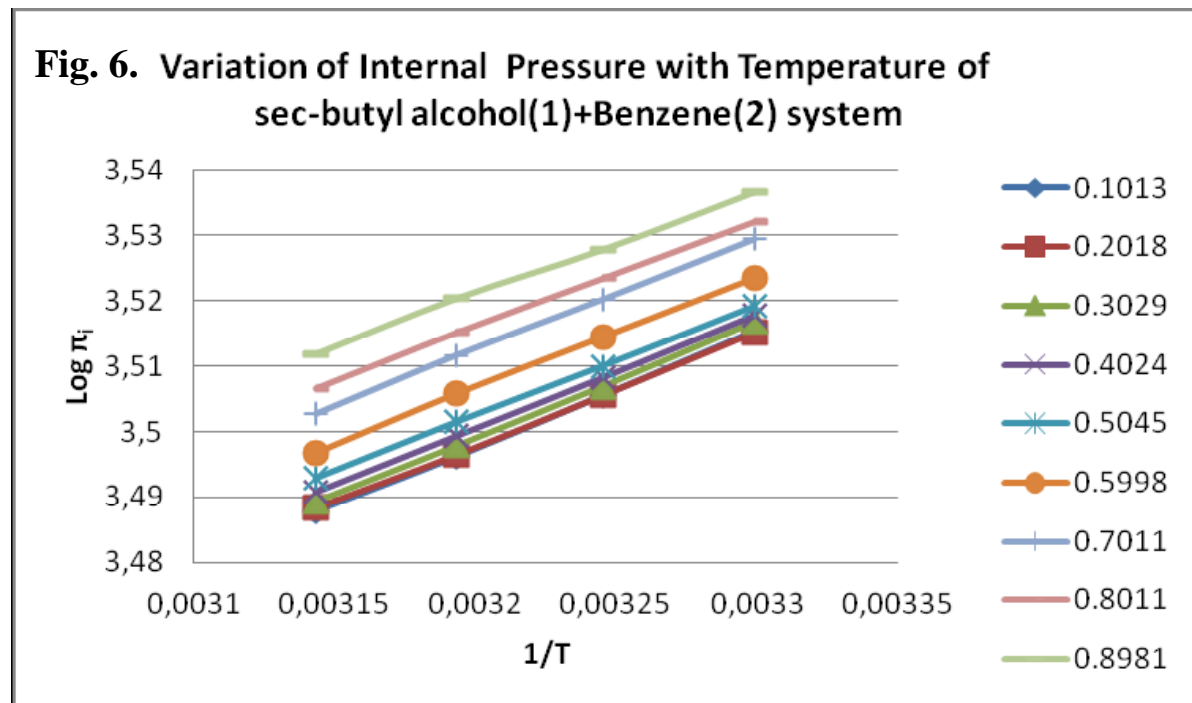
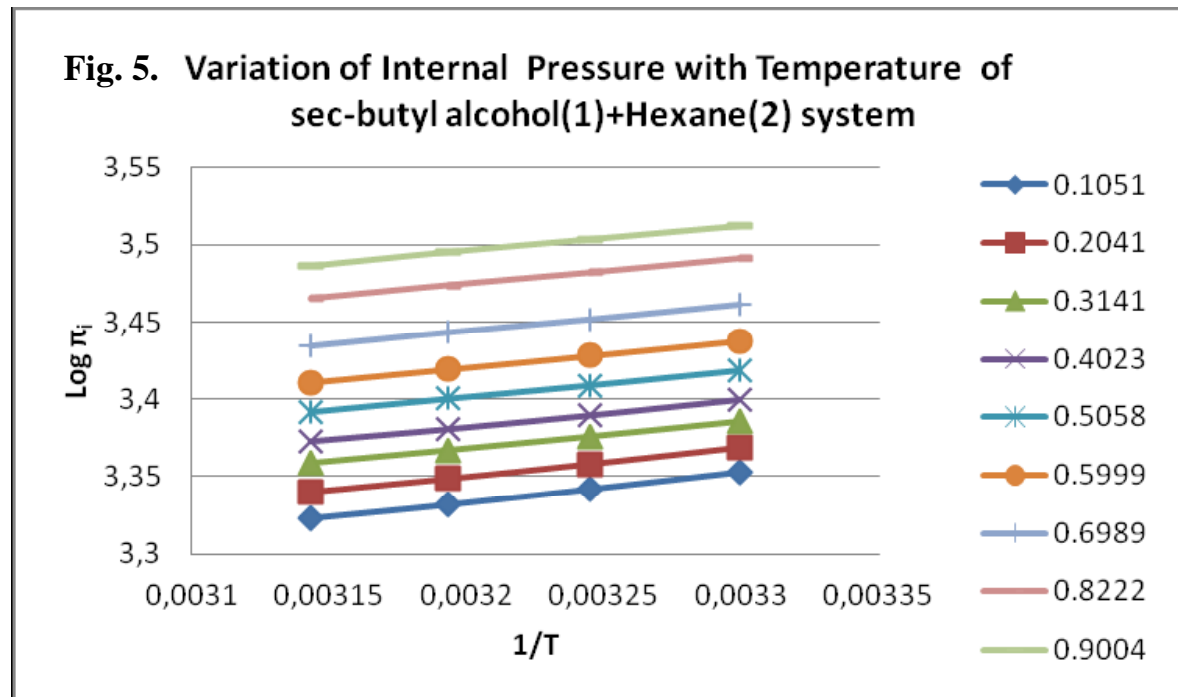


The average absolute deviation for the Ternary system is greater than that for the sub-binary system. This may be due to the Interaction between the three components. Among the three components, one of the component is self associated alcohol (sec-butyl alcohol). While the other two components (benzene and hexane) which are non-polar in nature.

Hexane is a non-polar chain molecule; only Vander Waals type interactions are present in hexane, while alcohol molecule is polar and associate strongly through hydrogen bonding. The alcohol molecule associate in inert hexane medium and form clusters. An associated molecular cluster in a liquid may be called as a quasi-molecule or a pseudo molecule¹⁹. While with benzene, π -bond interaction takes place with alcohol.

Due to these strong interactions among the components in a ternary liquid mixture, the interaction constant values for the Ternary liquid mixture increases than that of the

Binary liquid mixtures. This increase in Interaction constant values leads to increase in absolute average deviation for the Ternary system than that of the Binary system.



5. CONCLUSION

It is evident from the present work, that

- The absolute average deviation between the experimental and correlated values for the Binary system and Ternary system varies from 0.17% to 1.37% indicating the applicability of equations (4) and (5).
- Internal pressure and their use in the study of molecular interactions.
- The character of association of alcohols makes the study of interactions particularly interest.
- The cohesive forces are of primary importance.

REFERENCES

- [1] Barton, A.F.M., *J. Chem. Edu.* 48(3), (1971) 156
- [2] Vanderwaals, J.D., *Essay on the continuity of the gaseous and liquid states* London (1873).
- [3] Suryanarayana C.V., *J. Acoust. Soc. Ind.* 7 (1979) 131.
- [4] Suryanarayana C.V., *J Acoust Soc India* 5(4), (1977) 111
- [5] Hildebrand J.H., Scott R.L., *Solubility of Non-electrolytes*, 111rd Edn., Reinhold, Publ.Corp., New York, (1950), P.121.
- [6] Hildebrand J.H., Scott R.L., *Regular Solutions*, Prentice-Hall, Englewood cleffs, New Jersey, (1962).
- [7] Dack M.R.J., *Chem. Soc. Rev.* 4(2), (1975) 211
- [8] Stavely L.A.K., Lupman W.J., Hart K.R., *Faraday Trans. Soc. Diss.*, 15 (1953) 130
- [9] Richards T.W., *Chem. Rev.* 2 (1925) 315
- [10] Allen G., Gee G., Wilson G.J., *Polymer* 1 (1960) 456
- [11] Weissberger A., *Technique of organic chemistry* Vol.7(2nd edn), Interscience Newyork., (1955).
- [12] Srivastava S.C., Berkowitz N., *Canadian Journal of Chemistry*, 41 (1963) 177-1793
- [13] Amirthaganesan G., Govindasamy S., An Andiappan, *Indian Journal of Chemistry* Vol.25A (1986) 1023-1026
- [14] Rowlison J.S., *Liquid and Liquid mixtures*, 2nd Edn., Butter Worths, London, 159 (1969).

- [15] Marimuthu S., *Internal Pressure, Free Volume and Thermodynamic Studies of Molecular Interactions.*, M.Phil.Thesis, Department of Physics, Annamalai University (1987).
- [16] Rajendran V., *Ultrasonic studies on some Ternary systems and Rock Specimens*, Ph.D Thesis, Annamalai University (1992).
- [17] Kannappan A.N., Palani R., *Ind. J. Pure Appl. Phys.*, 45 (7), (2007) 573-579
- [18] Pugalendi K.V., *A study of internal pressure of Binary liquid Mixtures from Ultrasonic Measurements*, M.Phil Thesis, Annamalai University (1983).
- [19] Vasantharani P., Muthu Shailaja S., Kannappan A.N., Ezhil Pavai R., *Journal of Applied Sciences*, Vol.8, Issue:12, (2008) 2329-2332