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Chemical Physics

Elixir Chem. Phys. 33A (2011) 2349-2354

ISSN: 2229-712X

A study of internal pressures of ternary and sub-binary liquid mixtures at different temperature

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ARTICLE INFO

Article history:
Received: 22 February 2011;
Received in revised form:
18 March 2011;
Accepted: 28 March 2011;

Keywords
Ultrasonic velocity,
Density,
Molecular weight
Internal pressure.

ABSTRACT

Internal pressures of the ternary and sub-binary mixtures of Benzene(1)+Hexane(2) +n-Propanol(3) have been computed from ultrasonic velocity measurements at different mole fractions in the temperature range of 30^0C- 45^0C. The equation formulated by Andiappan et.al, for evaluating internal pressures of binary liquid mixtures has been modified and extended in the present work for the Ternary systems. The internal pressures computed with the help of the modified relation and showed close agreement with observed values. The absolute average deviation between the calculated and observed values from 1.7% to 1.9% for the ternary system studied.

Introduction

Comprehensive studies show that internal pressure is the single factor which varies due to all the internal forces like hydration, ion-solvent interaction and dielectric constant etc., both in electrolyte and non-electrolyte solutions. Internal pressure being a measure of cohesive forces acting in a liquid is sensitive to change of temperature, concentration and external pressure. In addition, properties such as solubilities[1, 2], surface tension, energy of viscous flow, dipole moments[3] have been discussed widely in terms of internal pressure.

Ultrasonic velocity measurements are highly sensitive to molecular interactions and can be used to provide qualitative information about the physical nature and strength of molecular interactions in liquid mixtures[4-6]. In recent years, the measurement of ultrasonic velocity has been successfully employed in understanding the nature of molecular interactions in pure liquids [7] and liquid mixtures[8-10].

The importance of internal pressure in understanding the properties of liquids and the full potential of internal pressure of as a structural probe did become apparent with the pioneering work of Hildebrand[11, 12] and the first review of the subject by Richards[13] appeared in 1925. In an excellent article Dack[14] reviewed the importance of solvent internal pressure and cohesion to solution phenomena. A review on the relationship between the intermolecular forces and properties was made by Kortum[15]; Barton[16] discussed the relationship between internal pressure and molar volume in some depth.

The present work has been carried out to study the variation of internal pressure with temperature and composition of binary and ternary liquid mixtures. The equation proposed by S.C.Srivastava and N.Berkowitz[17] was used to compute internal pressure from the measurement of ultrasonic velocity, density and molecular weight.

Materials and Methods

The liquids were purified as and when required as per the procedure recommended by Weissberger[18].

Analar grade benzene supplied by B.D.H. India and guaranteed. Reagent grade n-Hexane of Japan product was redistilled after drying with sodium. The fraction boiling at 80.1^0C and 68.7^0C respectively were collected and stored. Guaranteed reagent grade n-Propanol was treated with calcium chloride and distilled. The fraction distilling at 97.1^0C was collected. The physical constants of pure liquids are given in table-1.

Ultrasonic velocities of pure liquids and liquid mixtures in the temperature range of 30^0C to 45^0C were measured using an ultrasonic interferometer operating at 3MHz.

The density was determined at the experimental temperature using 10ml capacity specific gravity bottle immersed in a thermostatic bath (accuracy $+0.01^0$C). The volume of the bottle at the experimental temperatures, viz. 30^0C-45^0C was ascertained using doubly distilled water. The densities of water at these temperatures were obtained from literature. The viscosity of pure liquids and liquid mixtures at different temperatures were determined using an Ostwald viscometer.

Theory and Calculation

The internal pressure for pure liquids and mixtures at different temperatures were calculated using the equation (1) and (2)

$$\pi_i = \frac{UD}{K\sqrt{M}} \qquad \text{\_\_\_\_\_\_\_\_ (1)}$$

Where

π_i, U, D and M represent internal pressure, ultrasonic velocity, density and molecular weight of the pure component respectively. K was distinctly structure dependent constants

$$(\pi_i)_{12} = \frac{U_{12}D_{12}}{(X_1K_1 + X_2K_2)\sqrt{M_{12}}} \qquad \text{\_\_\_\_\_\_\_\_ (2)}$$

Where

$(\pi_i)_{12}$,, U_{12}, D_{12} and M_{12} represent internal pressure, ultrasonic velocity, density and molecular weight of the mixture respectively and x_1, x_2 are the molefractions of component 1 and 2.

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Suryanarayana and Kuppusamy[19] derived an expression to account for the variation of internal pressure with concentration of the electrolyte which is of the form, internal pressure of

$\pi = \pi_0 + Am^2 + \mathrm{Bm}$ ________ (3)

Where

π is the internal pressure of the solution, π_0 is the internal pressure of the solvent, m is molality and A, B are constants which are temperature dependent because of in adequacies of expression (3). It is modified and given by Andiappan et.al.,[20] in the form,

$\log\pi = x_1\log\pi_1 + x_2\log\pi_2 - \beta x_1x_2$ ________ (4)

Where x_1 and π_1 are the mole fraction and internal pressure of the component 1 and x_2 and π_2 are those of the component 2. The equation (4) containing only one constant β has been correlating the experimental data.

In the present work, the extension of equation (4) for ternary system is attempted and the equation is written in the modified form,

$\log\pi = x_1\log\pi_1 + x_2\log\pi_2 + x_3\log\pi_3 + x_1x_2(\beta_{12}(x_1-x_2)) + x_2x_3(\beta_{23}(x_2-x_3))$
$+ x_3x_1(\beta_{31}(x_3-x_1)) - C(x_1x_2x_3)$ _______(5)

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) and the constant C from equation (5). Eqn (5) containing the above constants have been employed for correlating the experimental data.

Results and Discussion

The experimentally determined internal pressure data for ternary as well as the sub-binary systems have been correlated through Eqns, (4) & (5) in the temperature range of 30^0C to 45^0C. Table 2 and 3 shows a comparison of experimental and calculated internal pressure values for Ternary and sub-binary mixtures respectively at various temperatures. The absolute average deviation between experimental and calculated values, ternary (C) and sub-binary (β) interaction constants are given in Table 2 and 3 respectively. The constants β and C have been determined through least square method at all temperatures. In both case, the binary and ternary interaction constants are not varied more when the temperature increases.

Internal pressure in all Binary mixtures

The absolute average deviation between the experimental and correlated values for the binary system varies from 0.12% to 0.3%. The quantitative relations between internal pressure and temperature & internal pressure and concentration have been established by graphical method.

Variation of Internal pressure with Concentration of Alcohol in all binary mixtures

Table (2) and (3) evident that the internal pressure increases with concentration of alcohols, because at higher alcohol concentration hydrogen bonding becomes predominant, resulting in the increase of the internal pressure. This is also evidenced by Figure 1-3. This suggests the close packing of the molecules, which may be brought about by increasing magnitude of interactions[21, 22]. Such a results are also evidenced by Rao et.al.,[23] in o-Chlorophenol system.

Variation of Internal pressure with Temperature in all Binary mixtures

Table (2) and (3) also shows the falling of internal pressure with increase of temperature is the important observation in all the cases studied, because the cohesive forces between molecules becoming less with increase of temperature. Figure 4-6 shows a linear variation of internal pressure with the reciprocal of temperature for Binary liquid mixtures in the temperature range 30^0C to 45^0C.

Internal pressure in Ternary mixture

The absolute average deviation between the experimental and correlated values for the Ternary system varies from 1.7% to 1.9%. In the ternary systems the deviation is greater when the alcohol concentration is high because of the domination of hydrogen bonding at higher alcohol concentration, resulting in the increase of the deviation.

Figure:1

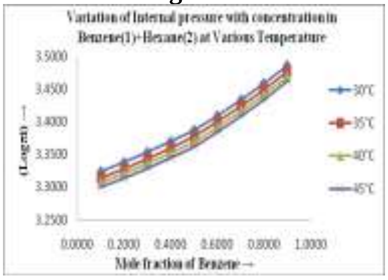


Figure:2

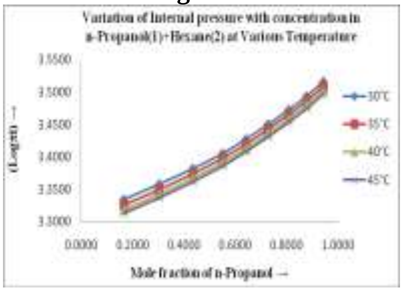


Figure:3

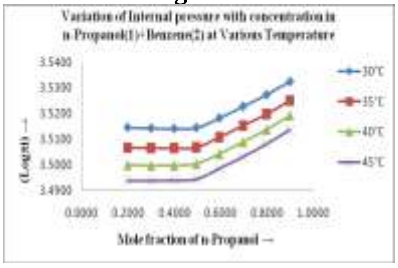


Figure:4

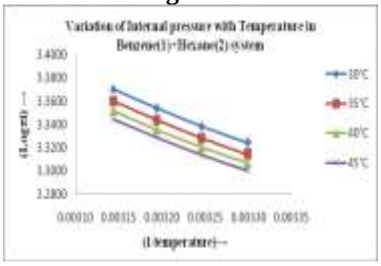


Figure:5

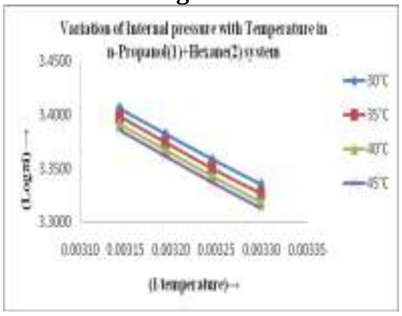
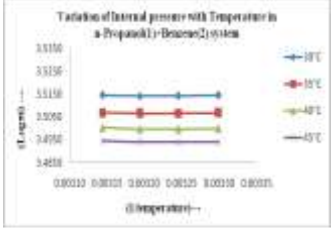


Figure:6



Conclusion

From the present investigation, it is eventually concluded that existence of the followings.

The absolute average deviation between the experimental and correlated values for the Ternary mixtures and Binary mixtures varies from 0.12% to 1.9%, indicating the applicability of equation (4) and (5). The effects of the concentration of Alcohol as a solute and the temperature effects on hydrogen bonds in the system are clearly seen. The role of hydrogen bonds and the structure of alcohols in interactions are observed. Finally we conclude that there exists a weak molecular association between the component molecules in Binary mixtures and also in Ternary mixtures.

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Table-1: The physical constants of pure liquids

LIQUID	DENSITY (Kgm^{-3})		BOILING POINT (°C)	
	Expl.	Lit.	Expl.	Lit.
	30^0C	25^0C	30^0C	25^0C
n-HEXANE	0.6493	0.6548	68.70	68.70
BENZENE	0.8675	0.8737	80.10	80.10
n-PROPANOL	0.7985	0.7995	97.10	97.20

Table 1 - Values of experimental & Calculated Internal pressure(in atm) for

Benzene(1)+Hexane(2)+n-Propanol(3)

Mole fraction		303.15K		308.15K		313.15K		318.15K	
X1	X2	Expl	calc	Expl	calc	Expl	calc	Expl	calc
0.0886	0.8061	2166.84	2257.42	2151.71	2226.07	2109.85	2187.29	2081.87	2160.03
0.2027	0.6921	2237.57	2332.69	2232.66	2312.84	2203.25	2271.89	2162.42	2244.50
0.3047	0.5950	2330.49	2403.57	2322.79	2388.59	2290.62	2345.77	2257.94	2317.45
0.4060	0.4953	2411.14	2485.72	2392.99	2472.24	2384.84	2427.49	2358.82	2397.62
0.5052	0.3955	2545.64	2606.01	2530.35	2592.86	2503.04	2546.34	2458.97	2515.02
0.6023	0.2981	2677.34	2762.42	2668.34	2747.33	2632.08	2699.25	2599.82	2666.49
0.7018	0.1979	2859.65	2940.88	2831.66	2918.90	2677.68	2869.30	2600.87	2834.30
0.8063	0.0959	3004.03	3137.71	2991.71	3101.38	2955.66	3050.28	2918.55	3011.85
0.1045	0.7046	2235.79	2336.58	2229.12	2314.56	2202.53	2274.04	2156.25	2246.31
0.2006	0.5975	2329.35	2377.34	2324.66	2371.74	2293.54	2328.92	2260.90	2301.49
0.3018	0.5024	2450.64	2429.90	2430.77	2433.02	2393.13	2388.16	2352.77	2360.17
0.4047	0.3980	2537.06	2517.14	2527.90	2523.46	2488.99	2476.53	2452.41	2447.08
0.5039	0.2986	2678.78	2668.59	2674.60	2673.92	2642.19	2625.37	2611.17	2594.49
0.6059	0.2000	2837.58	2859.10	2829.98	2854.97	2785.82	2805.03	2764.82	2771.68
0.7051	0.0993	3004.56	3090.58	2998.81	3066.80	2956.82	3015.70	2933.39	2978.43
0.1012	0.6007	2365.69	2424.65	2349.13	2408.72	2310.00	2366.82	2277.13	2338.19
0.2021	0.4986	2444.33	2443.06	2436.91	2447.19	2409.76	2402.80	2377.10	2374.83
0.3049	0.3995	2567.03	2495.97	2561.37	2509.84	2517.80	2463.28	2484.22	2434.75
0.4048	0.2991	2678.89	2615.71	2679.81	2630.92	2637.18	2582.52	2605.29	2552.56
0.5070	0.1976	2842.18	2814.79	2828.88	2821.24	2791.80	2771.30	2772.36	2738.81
0.6052	0.1006	3017.96	3056.85	3012.45	3041.30	2979.51	2990.44	2951.53	2953.91
0.0967	0.5081	2489.94	2513.89	2444.91	2500.21	2408.29	2457.37	2370.67	2427.64

0.2035	0.4042	2579.62	2530.15	2800.45	2538.52	2536.35	2492.93	2489.59	2463.94
0.3027	0.2996	2716.46	2626.85	2706.37	2642.07	2660.65	2594.12	2626.58	2563.99
0.4060	0.1999	2858.31	2795.53	2847.36	2805.66	2813.23	2756.14	2755.09	2723.93
0.5061	0.1003	3057.29	3041.50	3031.72	3029.66	3005.92	2979.29	2960.23	2943.04
0.1092	0.3967	2621.95	2644.52	2600.00	2634.34	2567.91	2589.96	2690.77	2558.80
0.2025	0.3009	2747.88	2702.88	2746.28	2708.60	2719.73	2661.58	2695.90	2630.40
0.3063	0.1991	2886.27	2837.14	2879.73	2843.78	2839.90	2794.81	2798.09	2762.00
0.4088	0.0984	3073.35	3059.55	3059.53	3047.10	3017.30	2997.32	2984.26	2960.84
0.1024	0.2963	2789.96	2837.25	2777.41	2820.93	2746.18	2775.40	2717.58	2741.75
0.1992	0.2018	2979.75	2914.54	2957.65	2909.54	2897.37	2861.64	2851.40	2827.48
0.3063	0.1031	3070.16	3093.51	3065.54	3078.54	3037.58	3029.45	3014.15	2992.62
0.0973	0.2135	2957.60	3010.11	2913.78	2985.71	2871.35	2939.54	2855.10	2903.52
0.1973	0.1086	3200.85	3149.33	3144.03	3126.25	3110.50	3078.25	3082.52	3040.54
0.0906	0.0991	3250.28	3256.95	3216.36	3217.06	3173.85	3170.62	3131.06	3130.95
		C=1.2657		C=0.9797		C=1.0113		C=0.9928	
		ABSD=1.9834		ABSD=1.9233		ABSD=1.7504		ABSD=1.8971	

Table 2 - Values of experimental & Calculated Internal pressure(in atm)

Benzene(1)+Hexane(2)

Molefraction	303.15K		308.15K		313.15K		318.15K	
(X1)	Expl	calc	Expl	calc	Expl	calc	Expl	calc
0.1016	2110.3	2102.2	2062.0	2057.8	2026.5	2020.1	1997.2	1991.4
0.2010	2180.3	2171.6	2130.1	2123.5	2092.1	2083.8	2060.1	2052.6
0.3010	2260.0	2252.9	2206.9	2201.3	2166.1	2159.7	2132.7	2125.9
0.4008	2345.5	2346.5	2291.0	2291.8	2248.1	2248.2	2212.1	2212.0
0.5017	2441.9	2455.2	2389.2	2397.7	2341.1	2352.1	2303.0	2313.5
0.6014	2569.9	2578.0	2514.6	2518.3	2464.8	2470.6	2425.1	2429.7
0.7033	2718.4	2721.1	2659.2	2659.9	2609.2	2609.9	2566.0	2566.8
0.7993	2876.6	2874.3	2812.8	2812.3	2760.3	2760.2	2714.6	2715.0
0.8998	3063.9	3055.2	2997.4	2993.2	2944.3	2938.9	2898.0	2891.8
	ß=0.0882 ABSD=0.2741		ß=0.0957 ABSD=0.1664		ß=0.0980 ABSD=0.2139		ß=0.1015 ABSD=0.2085	

n-Propanol(1)+Hexane(2)

Molefraction	303.15K		308.15K		313.15K		318.15K	
(X1)	Expl	calc	Expl	calc	Expl	calc	Expl	calc
0.1664	2162.1	2152.6	2119.8	2111.2	2082.7	2074.9	2054.3	2047.4
0.3032	2281.5	2269.6	2236.7	2227.1	2199.5	2190.0	2170.0	2161.1
0.4344	2411.4	2407.7	2366.6	2363.6	2328.3	2325.4	2297.6	2295.0
0.5499	2544.8	2553.3	2500.9	2507.3	2461.7	2468.0	2430.4	2436.0
0.6409	2677.1	2686.2	2630.4	2638.2	2590.7	2597.9	2557.7	2564.5
0.7274	2822.3	2829.2	2773.7	2778.9	2732.4	2737.6	2697.1	2702.6
0.8070	2970.7	2976.8	2920.1	2924.0	2877.7	2881.7	2840.2	2845.1
0.8770	3118.8	3120.6	3065.0	3065.3	3021.0	3022.0	2981.8	2984.0
0.9427	3284.6	3268.9	3223.1	3210.8	3179.2	3166.6	3139.5	3127.1
	ß=0.1028 ABSD=0.3092		ß=0.1014 ABSD=0.2468		ß=0.1018 ABSD=0.2481		ß=0.1022 ABSD=0.2446	

n-Propanol(1)+Benzene(2)

Molefraction	303.15K		308.15K		313.15K		318.15K	
(X1)	Expl	calc	Expl	calc	Expl	calc	Expl	calc
0.1980	3270.2	3262.5	3212.0	3205.7	3161.9	3154.7	3118.3	3112.1
0.2992	3268.0	3262.0	3211.1	3205.3	3160.1	3155.2	3118.5	3112.7
0.3990	3266.9	3268.5	3210.3	3211.8	3160.7	3162.6	3119.3	3120.1
0.4944	3269.6	3281.2	3212.6	3224.6	3165.0	3176.1	3122.5	3133.6
0.5939	3297.9	3301.2	3242.5	3244.7	3193.7	3196.9	3152.4	3154.4
0.6961	3332.4	3329.1	3276.3	3272.7	3227.3	3225.7	3185.5	3183.1
0.7974	3367.1	3364.4	3310.2	3308.1	3263.4	3261.7	3221.7	3219.0
0.8985	3407.2	3407.4	3351.1	3351.2	3305.3	3305.4	3262.8	3262.6
	ß=0.0460 ABSD=0.1353		ß=0.0468 ABSD=0.1296		ß=0.0471 ABSD=0.1258		ß=0.0475 ABSD=0.1255	