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A Study of Internal Pressures of Binary Liquid Mixtures at Different Temperatures

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Internal pressures of the binary systems chlorobenzene-*n*-propanol, chlorobenzene-isopropanol and chlorobenzene-*n*-butanol have been evaluated from ultrasonic velocity measurements at different mol fractions in the temperature range of 30°-55°C. An equation for theoretically evaluating internal pressures of binary liquid mixtures has been suggested. The internal pressures calculated with the help of the proposed equation agree closely with the experimental values. The absolute deviation between the experimental data and correlated values varies from 0.4 to 2.7%.

Extensive studies have been made during the past decades to confirm the fact that internal pressure is the significant factor in determining the behaviour of liquids of all types. Suryanarayana and Kuppusamy[1,2] evaluated the internal pressures of different liquids and solutions of electrolytes. Internal pressure, being a measure of cohesive forces[3] acting in a liquid, is sensitive to change of temperature, concentration and external pressure. The present work has been carried out to study the variation of internal pressure with temperature and composition of polar binary liquid mixtures. The equation proposed by Suryanarayana and Kuppusamy[2] was used to compute internal pressures from measurements of viscosity, ultrasonic velocity and density.

Materials and Methods

The liquids were purified as and when required as per the procedure recommended by Weissberger[4].

Chlorobenzene, *n*-propanol and isopropanol (all BDH, AR) were dried over anhydrous calcium chloride for 24 hr and distilled. The middle cuts boiling respectively at 131.6°-31.8°, 97°-97.2° and 82-82.5° were collected and stored. *n*-Butanol (BDH, AR) was dried over anhydrous potassium carbonate and the fraction distilling at 117.7°-17.9° was collected.

Physical constants of pure liquids are given in Table 1.

Density, viscosity and ultrasonic velocity measurements

Densities of pure liquids and liquid mixtures were measured using a specific gravity bottle (10 ml capacity). The volume of the bottle at the experimental temperatures, viz. 30°-55°C, was ascertained using doubly distilled water. The densities of water at these temperatures were obtained from literature[5].

Viscosities of liquids and liquid mixtures in the temperature range 30°-55°C were measured using a Ostwald viscometer.

Ultrasonic velocities in liquids and liquid mixtures in the temperature range 30°-55°C were measured using an ultrasonic interferometer operating at 2 MHz.

Internal pressure determination

Internal pressures of liquids and liquid mixtures were computed using Eq. (1)

$$\pi = bRT\left(\frac{K\eta}{u}\right)^{1/2}\frac{\rho^{2/3}}{M^{7/6}} \qquad \ldots (1)$$

where π = internal pressure in atm.; b = packing factor, which is equal to 2 assuming cubic packing, R = gas

Table 1—Physical Constants of Pure Liquids

Liquid	Density g/ml		Refractive index		Boiling point (°C)	
	Expl (30°C)	Lit (20°C)	Expl (30°C)	Lit (20°C)	Expl	Lit
Chlorobenzene	1.0924	1.106	1.5160	1.5251	131.6-131.8	132.0
n-Butanol	0.8027	0.810	1.3930	1.3991	117.7-117.9	117.7
n-Propanol	0.7983	0.804	1.3780	1.3854	97.0-97.2	97.2
Isopropanol	0.7822	0.785	1.3710	1.3776	82.0-82.5	82.4

Table 2—Values of Experimental and Calculated Internal Pressures (in atms) for Chlorobenzene + Alcohols

Mol fr (x_1)	30°		35°		40°		45°		50°		55°	
	Expl	Calc	Expl	Calc	Expl	Calc	Expl	Calc	Expl	Calc	Expl	Calc
	Chlorobenzene (2)-*n-propanol* (1)											
0.1039	3672.28	3675.93	3586.65	3618.35	3539.63	3623.01	3452.14	3499.85	3378.01	3428.86	3350.39	3356.22
0.1949	3902.62	3875.89	3798.77	3797.67	3722.78	3778.16	3614.42	3631.28	3526.08	3544.38	3501.79	3494.38
0.2922	4111.99	4141.09	3998.22	4028.41	3920.05	3991.28	3809.21	3818.30	3709.74	3712.36	3649.77	3680.61
0.3928	4467.99	4480.21	4340.14	4329.91	4208.90	4270.71	4074.31	4069.49	3967.19	3941.04	3888.84	3921.03
0.4908	4870.76	4886.82	4802.63	4696.26	4562.69	4610.73	4396.56	4379.86	4229.10	4225.81	4144.64	4209.50
0.5932	5382.27	5408.05	5178.81	5171.43	5030.48	5051.61	4831.21	4787.18	4618.50	4601.40	4532.74	4578.57
0.6916	6042.42	6023.26	5734.86	5736.57	5556.70	5575.07	5347.58	5275.46	5119.29	5052.78	4981.92	5011.06
0.7956	6814.21	6823.39	6477.93	6477.17	6217.91	6259.22	5917.44	5918.75	5677.12	6222.43	6109.61	5568.78
0.8974	7822.64	7794.55	7417.99	7377.60	7103.48	7091.37	6749.53	6706.87	6412.72	6378.23	6134.99	6237.20
	$\beta=0.2257$		$\beta=0.2437$		$\beta=0.2385$		$\beta=0.2563$		$\beta=0.2585$		$\beta=0.2088$	
	ABSD = 0.4%		ABSD = 0.5%		ABSD = 0.9%		ABSD = 0.6%		ABSD = 1.8%		ABSD = 2.1%	
	Chlorobenzene (2)-*Isopropanol* (1)											
0.0978	3625.03	3567.40	3535.01	3504.84	3515.76	3523.09	3425.97	3432.10	3346.06	3365.39	3319.70	3287.10
0.1990	3788.97	3704.46	3684.78	3595.41	3616.49	3613.27	3530.08	3521.72	3449.56	3439.83	3408.56	3381.59
0.2966	4024.68	3905.31	3903.54	3754.49	3811.71	3760.93	3705.30	3662.49	3617.60	3562.93	3577.05	3516.93
0.4002	4296.46	4203.24	4154.07	4010.12	4077.67	3990.33	3918.68	3876.75	3830.49	3754.21	3774.71	3713.18
0.4996	4648.03	4588.20	4474.27	4355.56	4374.53	4292.97	4230.42	4155.57	4055.65	4005.53	3978.70	3960.49
0.5954	5029.79	5071.98	4878.69	4802.10	4720.38	4676.27	4544.58	4504.86	4362.44	4321.66	4272.28	4262.87
0.6995	5661.77	5755.93	5382.74	5447.20	5222.83	5218.43	4991.95	4993.72	4737.27	4764.64	4632.05	4676.80
0.7999	6424.57	6616.51	6088.72	6273.84	5798.29	5897.51	5515.90	5599.40	5266.80	5313.09	5069.14	5178.64
0.8991	7504.55	7721.10	7017.19	7352.26	6671.63	6762.23	6300.37	6362.05	5939.47	6002.22	5713.75	5797.10
	$\beta=0.3667$		$\beta=0.4172$		$\beta=0.3498$		$\beta=0.3198$		$\beta=0.3138$		$\beta=0.2655$	
	ABSD = 2.1%		ABSD = 2.7%		ABSD = 1.1%		ABSD = 0.9%		ABSD = 1%		ABSD = 1.2%	
	Chlorobenzene (2)-*n-butanol* (1)											
0.1057	3623.63	3651.52	3526.15	3596.29	3475.20	3568.59	3394.35	3470.67	3316.79	3400.11	3290.49	3317.36
0.2008	3777.47	3832.72	3686.30	3738.33	3601.32	3679.50	3506.27	3576.46	3429.63	3490.14	3390.63	3421.86
0.3003	4033.91	4068.09	3870.86	3933.41	3815.69	3842.64	3709.16	3729.86	3610.24	3625.40	3563.43	3566.51
0.3997	4329.88	4358.24	4174.50	4182.41	4069.48	4059.66	3943.15	3931.95	3817.10	3807.05	3749.15	3751.26
0.5009	4706.00	4720.06	4524.80	4500.64	4394.31	4344.63	4227.21	4168.85	4076.65	4046.40	3985.46	3986.44
0.5995	5122.71	5149.23	4895.89	4885.10	4740.51	4695.47	4545.11	4517.13	4372.12	4340.99	4270.63	4268.46
0.7007	5730.54	5684.48	5442.94	5371.58	5235.39	5145.73	4978.91	4927.36	4781.19	4717.98	4636.68	4621.69
0.8003	6432.32	6325.14	6099.51	5960.98	5830.20	5697.45	5533.98	5426.47	5283.11	5139.81	5083.57	5044.29
0.8984	7176.92	7091.50	6760.95	6673.46	6444.56	6370.75	6097.31	6031.07	5804.63	5735.46	5590.81	5547.83
	$\beta=0.2055$		$\beta=0.2320$		$\beta=0.2548$		$\beta=0.2374$		$\beta=0.2396$		$\beta=0.2008$	
	ABSD = 0.9%		ABSD = 1.2%		ABSD = 1.4%		ABSD = 1.2%		ABSD = 1.3%		ABSD = 0.4%	

constant in J/K/mol; ρ = density in g/ml; K = a constant ($=4.28\times10^9$); u = ultrasonic velocity in cm/sec; η = viscosity in poises; T = absolute temperature; and M = molecular weight of the liquid.

Results and Discussion

While studying the behaviour of aqueous electrolyte solutions Suryanarayana and Kuppusamy[2] derived expression (2) to account for the variation of internal pressure with the concentration of the electrolyte.

$$\pi=\pi_0+Am^2+Bm \qquad \ldots (2)$$

where π = the internal pressure of the solution; π_0 = the internal pressure of the solvent; m = the molality; and A and B = constants which are temperature-dependent.

We tried to extend Eq. (2) to study the behaviour of binary liquid mixtures. Because of inadequacies of expression (2), this expression was modified to Eq. (3)

$$\log\pi=\log\pi_2+\alpha x_1+\beta x_1^2 \qquad \ldots (3)$$

where π = the internal pressure of the liquid mixture; π_2 = the internal pressure of the component-2; x_1 = the mol fraction of the component-1 and α and β = constants which are temperature-dependent.

From Eq. (3) it is evident that the variation of internal pressure with concentration is quadratic in nature. When $x_1=1$, π becomes equal to π_1, the internal pressure of component-1 and Eq. (3) reduces to Eq. (4)

$$\log\pi_1=\log\pi_2+\alpha+\beta \qquad \ldots (4)$$

so that,

$$(\alpha+\beta)=\log\pi_1-\log\pi_2 \qquad \ldots (5)$$

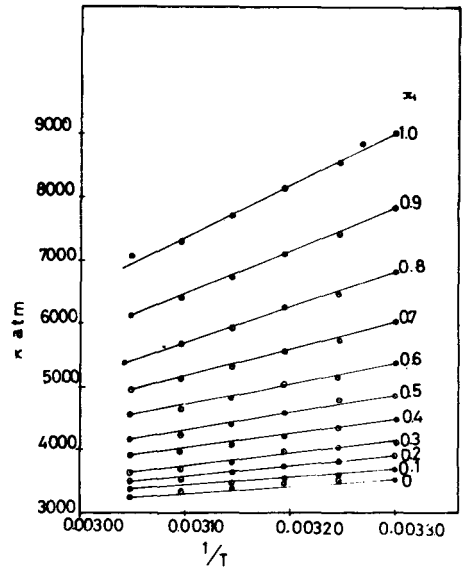

Fig. 1—Variation of Internal Pressure with Temperature for the binary liquid system Chlorobenzene (2)-*n*-Propanol (1)

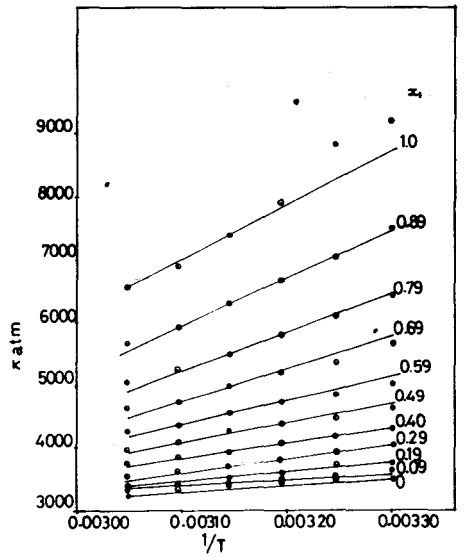

Fig. 2—Variation of Internal Pressure with Temperature for the binary liquid system Chlorobenzene (2)-Isopropanol (1)

Equation (3) can be rewritten as,

$$\log \pi = \log \pi_2 + \alpha x_1 + \beta x_1 - \beta x_1 + \beta x_1^2$$
$$= \log \pi_2 + x_1(\alpha + \beta) - \beta x_1(1 - x_1) \quad \ldots (6)$$

Substituting the value of $(\alpha + \beta)$ from Eq. (5) into Eq. (6) we get,

$$\log \pi = \log \pi_2 + x_1 \log \pi_1 - x_1 \log \pi_2 - \beta x_1(1 - x_1)$$
$$= x_1 \log \pi_1 + \log \pi_2(1 - x_1) - \beta x_1(1 - x_1) \quad \ldots (7)$$

But $(1 - x_1) = x_2$. Therefore Eq. (7) becomes,

$$\log \pi = x_1 \log \pi_1 + x_2 \log \pi_2 - \beta x_1 x_2 \quad \ldots (8)$$

Equation (8) containing only one constant (β) has been employed for correlating the experimental data.

The experimentally determined internal pressure data for all the three systems have been correlated through Eq. (8) at temperatures 30° to 55°C (Table 2). Constant β has been determined through a least square method at all the temperatures. It is evident from Table 2 that the internal pressure increases with increase in the concentration of alcohols, probably because at higher alcohol concentration hydrogen bonding becomes predominant resulting in the increase of the internal pressure.

Further, it may be observed that the absolute deviation between the experimental data and correlated values varies from 0.4 to 2.7%, indicating applicability of Eq. (8). The value of β varies from 0.2 to 0.26 in the temperature range 30° to 55°C for the binary liquid mixtures involving normal alcohols namely, *n*-propanol and *n*-butanol while it varies from 0.31 to 0.42 for mixtures involving isopropanol. In the absence of more experimental data it is difficult to arrive at any definite conclusion in this regard.

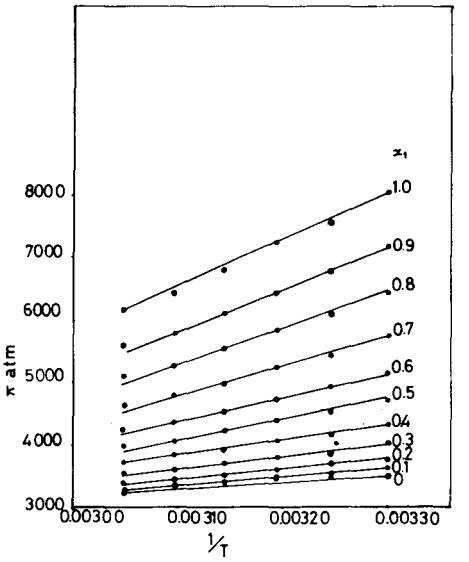

Fig. 3—Variation of Internal Pressure with Temperature for the binary liquid system Chlorobenzene (2)-*n*-Butanol (1)

Figures 1-3 show a linear variation of internal pressure with the reciprocal of temperature for pure liquids as well as liquid mixtures in the temperature range 30°-55°C. This linear variation may be represented by an equation of the type $(d\pi/dT) = -m/T^2$, where m is a constant depending on concentration. The values of m for chlorobenzene, *n*-butanol, *n*-propanol and isopropanol are: 1111100, 7575681, 8602064 and 9166500 respectively. It is found that internal pressure decreases with increase in temperature in all the cases or in other words cohesive forces[3] decrease with increase in temperature. It is also

observed in all the three systems that the internal pressures of the alcohols are greater than that of chlorobenzene. This may be attributed to the presence of H-bonding in alcohols.

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