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THEORETICAL ESTIMATION OF INTERNAL PRESSURE AND EXCESS INTERNAL PRESSURE IN BINARY LIQUID MIXTURES

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ABSTRACT:-

In recent years, in the study of molecular interactions in binary liquid mixtures by acoustical methods, internal pressure has gained significant interest. Several attempts have been made to calculate the internal pressure of liquids and liquid mixtures theoretically. Here we made use of two empirical methods to estimate the internal pressure in four binary liquid mixtures viz., cyclohexanone with isopropyl acetate and isobutyl acetate and N,N-Dimethyl acetamide with o-cresol and m-cresol. The ultrasonic velocity (U), density (ρ) and viscosity (η) have been measured for the said binary mixtures at 308 K. Excess internal pressure has also been calculated from the experimental data of pure liquids and liquid mixtures. The excess values give better understanding of the molecular interactions between the components.

Key Words: Ultrasonic velocity, binary liquid mixtures, internal pressure, molecular interactions.

INTRODUCTION:

In recent years, ultrasonic technique has become a powerful tool for studying the molecular behaviour of liquid mixtures[1-3]. This is because of its ability of characterizing physico - chemical behaviour of liquid medium[4-6]. The measurement of ultrasonic velocity have been adequately employed in understanding the molecular interactions in liquid mixtures. Molecular interaction studies can be carried out by both spectroscopic and non–spectroscopic techniques. However, ultrasonic velocity and viscosity measurements have been widely used in the field of interactions and structural aspect evaluation studies.

Internal pressure has gained significant interest by chemists, physicists and chemical engineers in past, as it provides a measure of explaining molecular interactions, internal structure, clustering phenomenon and dipolar interactions. Internal pressure has been a subject of active interest among several researchers during recent past[7–10]. Several attempts have been made by a number of investigators[11–16] to calculate the internal pressure of liquids and liquid mixtures theoretically.

The measurement of internal pressure is important in the study of the thermodynamic properties of liquids. The internal pressure is the cohesive force, which is a resultant of force of attraction and force of repulsion between the molecules17[-18]. Cohesion creates a pressure within the liquid. So internal pressure gives an idea of the solubility characteristics. Dissolved solutes exist under the internal pressure of the medium and their interactions with the solvent arise through hydrogen bonding, charge transfer, Columbic (or) Vanderwaal's interaction. The term a/v^2 in Vanderwaal's[19] equation being the measure of attractive force of the molecule is called the cohesive (or) internal pressure.

In order to understand more about the nature of interaction between the components of liquid mixtures, it is necessary to discuss the same in terms of excess parameters rather than actual values. They can yield an idea about the non linearity of the system as association or other type of interactions[20].

THEORITICAL:

The internal pressure is the single factor which varies due to all type of solvent-solute, solute-solute and solvent-solvent interactions. A general method of measuring the internal pressure based on the Maxwell's equation of thermodynamics[21] is

(1)

On the basis of statistical thermodynamics, expression for the determination of internal pressure by the use of free volume concept as given by

$$v_f = \frac{1}{V^2}\left[\frac{bRT}{P+\left(\frac{\delta E}{\delta v}\right)_T}\right]^3 \quad (2)$$

(2)

As is the internal pressure and neglecting P which is insignificantly small to

If the equation can be written as,

$$v_f = \frac{1}{V^2}\left[\frac{bRT}{\pi_i}\right]^3 \quad (3)$$

(3)

The final equation for the evaluation of internal pressure can be obtained by combining and rearranging the equations (6) and (7)

$$\pi_i = bRT\left(\frac{K\eta}{U}\right)^{\frac{1}{2}}\left(\frac{\rho^{\frac{2}{3}}}{M_{eff}^{\frac{7}{6}}}\right) \quad (4)$$

(4)

Where K is a constant and its value is 4.28 X 10^9 for all liquids., T the absolute temperature, η , the viscosity in NSm^{-2}, U, the ultrasonic velocity in ms^{-1}, ρ, the density in kgm^{-3} of the liquid.

Thermodynamically, the internal pressure is given by,

$$\pi_i = \left(\frac{\alpha T}{\beta_T}\right) \quad (5)$$

(5)

Empirical formula for α and at in terms of ultrasonic velocity (U), density ( ) and temperature (T) is as follows

$$\alpha = \left(\frac{75.6x10^{-3}}{T^{\frac{1}{9}}.U^{\frac{1}{2}}.\rho^{\frac{1}{3}}}\right) \quad (6)$$

(6)

$$\beta_T = \left[\frac{1.71x10^{-4}}{T^{\frac{4}{9}}U^{2}.\rho^{\frac{4}{3}}}\right] \quad (7)$$

(7)

With the help of equations (6) and (7) equation (5) can be written as

$$\pi_i = \left(44.2xT^{\frac{4}{3}}.U^{\frac{3}{2}}.\rho\right) \quad (8)$$

(8)

The above given equations (4) and (8) are very useful in direct computing the value of internal pressure from the experimental values of velocity, density and viscosity of binary liquid mixtures

The excess internal pressure is defined as the difference between the internal pressure $\pi_{i(mix)}$ of liquid mixture and that of an ideal mixture of the same compositions and is given by the relation

$$\pi_i^E = \pi_{i(mix)} - (X_1 \pi_{i(1)} + X_2 \pi_{i(2)}) \quad (9)$$

where X_1 & X_2 are the molefraction of the liquid components and $\pi_{i(1)}$ & $\pi_{i(2)}$ are the internal pressure of the corresponding liquids.

EXPERIMENTAL:

The four Liquid mixtures taken for study are:

System-1: Cyclohexanone + Isopropyl Acetate (CY + IPA)

System-2: Cyclohexanone + Isobutyl Acetate (CY+IBA)

System-3: NN Dimethyl Acetamide + o-cresol (NNDA + OC)

System-4: NN Dimethyl Acetamide + m-cresol (NNDA + MC)

All the chemicals used in the present research work are analytical reagent (AR) of minimum assay of 99.9% obtained from E-Merck, Germany and Sd.Fine chemicals, India, which are used without further purification. The purities of the above chemicals were checked by density determination at 308 ± 0.1K which showed an accuracy of $\pm 1 \times 10^{-4}$ kgm^{-3}. The binary liquid mixtures of different known compositions were prepared in stopper measuring flasks.

The ultrasonic velocity was measured at 308 K using a single crystal variable path interferometer operating at a frequency of 2MHz (MITTAL ENTERPRISES, New Delhi, Model: F-81) with an overall accuracy of ± 0.1% has been used. The density was measured at 308 K using specific gravity bottle by the standard procedure and the viscosity was measured at 308 K using Ostwald’s viscometer with an accuracy of ± 0.001 NSm^{-2}. An electronically digital operated constant temperature bath has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature 308 K with an accuracy of ± 0.1 K.

RESULTS AND DISCUSSION:

The following table shows the experimental values of ultrasonic velocity (U), density(ρ) and viscosity (η). Also the calculated internal pressure π_i by both the methods and values of the excess internal pressures π_i^E are reported. Fig.1 & Fig.2 shows the variation of π_i^E with mole fraction of cyclohexanone where as Fig.3 & Fig.4 shows the variation of π_i^E with mole fraction of NN-Dimethyl Acetamide which were calculated from both the equations (4) & (8).

The internal pressure is a cohesive force, which is the result of attractive and repulsive forces between the molecules. The attractive forces mainly consist of hydrogen bonding, dipole-dipole, and dispersion interactions. Repulsive forces, acting over very small intermolecular distances, play a minor role in the cohesion process under normal circumstances.

For the binary systems 1 & 2 viz., cyclohexanone + Isopropyl acetate & cyclohexanone + Isobutyl acetate the excess internal pressure vales are negative and decreasing with the increase in molefraction of cyclohexanone up to the molefraction (0.6) and then increases with increase in molefraction. This negative trend in π_i^E indicate that the only dispersion and dipolar forces operating with complete absence of specific interaction.

Table:1 Experimental value of ultrasonic velocity (U), density(ρ) and viscosity (η). calculated internal pressure π_i by both the equations and values of the excess internal pressures π_i^E

Molefraction X_1	**ρ** **Kg-m^{-3}**	**η** **X10^{-3}** **N-S-m^{-2}**	**U** **m-sec^{-1}**	**π_i** **X 10^{12}** **N-m^{-2}** Esq. (4)	**π_i** **X 10^{12}** **N-m^{-2}** Esq.(8)	**π_i^E** **X10^{11}** **N-m^{-2}** Esq. (4)	**π_i^EX10^{11}** **N-m^{-2}** Esq. (8)
Cyclohexanone + Isopropyl Acetate							
0.0000	854.6	0.5019	1058.8	0.9260	2.6502	0.0000	0.0000
0.1123	860.9	0.5229	1072.1	0.9487	2.7202	-1.1205	-0.5611

0.2218	867.4	0.5451	1085.5	0.9724	2.7923	-2.1749	-1.0937
0.3284	874.1	0.5711	1101.5	0.9980	2.8763	-3.0629	-1.5861
0.4321	880.5	0.6082	1120.8	1.0309	2.9738	-3.7686	-1.9853
0.5329	887.8	0.6644	1151.9	1.0737	3.1241	-3.8995	-2.2651
0.6312	896.6	0.7494	1188.9	1.1350	3.3083	-3.6511	-2.3422
0.7270	906.9	0.8650	1228.6	1.2142	3.5154	-3.1341	-2.2236
0.8202	917.6	1.0190	1272.4	1.3108	3.7487	-2.3113	-1.9115
0.9113	928.5	1.2430	1318.8	1.4395	4.0026	-1.2491	-1.2650
1.0000	939.1	1.6100	1366.8	1.6282	4.2713	0.0000	0.0000
Cyclohexanone + Isobutyl Acetate							
0.0000	855.9	0.5845	1104.3	0.8429	2.8271	0.0000	0.0000
0.1259	862.1	0.6009	1120.4	0.8724	2.9101	-0.9884	-0.6936
0.2452	868.1	0.6196	1134.8	0.9042	2.9870	-1.9420	-1.3128
0.3579	874.1	0.6467	1149.1	0.9421	3.0647	-2.7929	-1.8182
0.4642	880.6	0.6787	1161.8	0.9847	3.1388	-3.5869	-2.2279
0.5652	887.6	0.7233	1181.4	1.0337	3.2442	-3.9920	-2.5308
0.6610	895.1	0.7972	1213.8	1.0976	3.4071	-3.7436	-2.6431
0.7521	903.6	0.9001	1251.5	1.1771	3.6009	-3.1209	-2.5601
0.8389	913.9	1.0410	1290.6	1.2789	3.8140	-2.2468	-2.2278
0.9213	926.1	1.2510	1329.8	1.4177	4.0423	-1.1534	-1.4871
1.0000	939.1	1.6100	1366.8	1.6282	4.2713	0.0000	0.0000
NN-Dimethyl Acetamide + O-cresol							
0.0000	1035	6.5000	1453	3.0236	5.1598	0.0000	0.0000

0.0740	1033	6.9000	1467	3.1492	5.2245	2.5413	1.1539
0.1500	1030	7.7000	1479	3.3656	5.2733	6.0259	2.1639
0.2200	1023	8.5000	1486	3.5701	5.2747	9.2872	2.6579
0.3560	1017	8.2000	1489	3.6051	5.2597	12.0013	3.4403
0.4220	1011	6.9000	1487	3.3500	5.2181	10.5972	3.4773
0.5260	1001	5.2000	1475	2.9771	5.1041	8.6749	3.0504
0.6250	989.0	3.8000	1454	2.6078	4.9356	6.7028	2.0444
0.7530	969.0	2.4000	1436	2.1273	4.7462	4.1223	1.0290
0.8780	949.0	1.4900	1428	1.7145	4.6095	2.1657	0.5188
1.0000	924.0	0.8100	1425	1.2859	4.4739	0.0000	0.0000
NN-Dimethyl Acetamide + m-cresol							
0.0000	1012	8.6000	1475	4.3800	5.1602	0.0000	0.0000
0.0800	1011	9.4000	1483	4.4600	5.1971	3.5300	0.9180
0.1490	1010	10.100	1490	4.5200	5.2287	6.4900	1.7100
0.2220	1008	10.010	1497	4.4000	5.2552	7.7200	2.4700
0.3630	1003	8.8000	1498	3.9600	5.2344	8.0900	3.2300
0.4320	999	7.7000	1496	3.6300	5.2031	7.1400	3.3900
0.5330	993	5.9000	1489	3.0900	5.1355	5.1700	3.4100
0.6310	984	4.4000	1474	2.6000	5.0123	3.5900	2.8500
0.7580	969	2.9000	1454	2.0400	4.8358	2.2700	1.9600
0.8200	958	2.3000	1444	1.7900	4.7316	1.7900	1.3400
1.0000	924	0.8100	1425	0.9990	4.4739	0.0000	0.0000

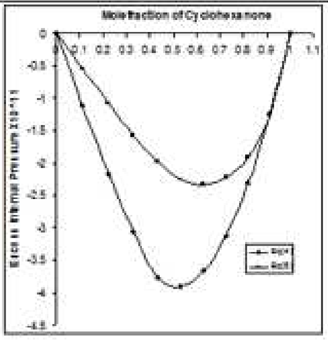

Fig.1: Variation of Excess internal Pressure for binary system-1.

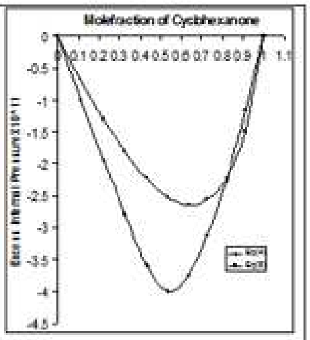

Fig.2: Variation of Excess internal Pressure for binary system-2.

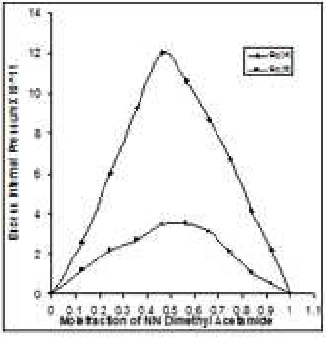

Fig.3: Variation of Excess internal Pressure for binary system-3.

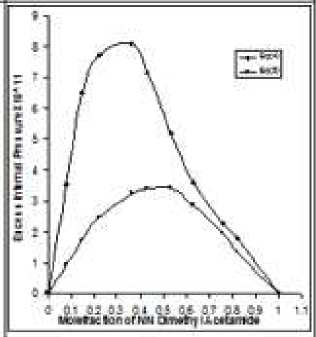

Fig.4: Variation of Excess internal Pressure for binary system-4.

For the binary systems 3 & 4 viz., NN Dimethyl Acetamide + o-cresol & NN Dimethyl Acetamide + m-cresol the excess internal pressure values are positive and increasing with the increase in molefraction of cyclohexanone up to the molefraction (0.5) and then decreases with increase in molefraction. Here the positive trend indicates specific interactions between the solute and solvent molecules controlled by the formation of complex bond through O-H…O hydrogen bonding. However the values obtained by equation (4) are found to be greater than equation (8).

CONCLUSION:

Both the theoretical treatments give satisfactory results. This approach offers simple methods to describe the molecular interactions in the liquid mixtures.

Excess internal pressure π_i^E can be used as a tool to predict the intermolecular interactions because it deals with the basic cohesive forces which are the resultant of forces of repulsion or forces of attraction among the molecules.

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