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Isothermal compressibility studies of binary solution of cycloheptane and methanol

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Abstract
Density and ultrasonic velocity data have been employed for the calculation of isothermal compressibility values (κ_T). Significance of the study of cohesive forces in the light of internal pressure has been emphasized during recent years. The internal pressure (P_i) and Pseudo-Gruneisen parameter (Γ) values have been computed by using the values of κ_T. The trend of variation in internal pressure and Pseudo-Gruneisen parameter reflects the disruption of molecular association due to a decrease in kinetic energy of constituents of solutions.

Keywords: Isothermal compressibility, internal pressure, cycloheptane, methanol

Introduction
The equilibrium properties of a liquid are strongly dependent on its structure which depends upon the forces between molecules. In general, it changes with composition and temperature which, in turn, is reflected in the thermodynamic properties of solutions.
Isothermal compressibility, Internal pressure are the key parameters in molecular thermodynamics of fluid phase equilibria. These parameters can be deduced by measuring the ultrasonic velocity and density. The ultrasonic velocity and density data of solutions are employed to determine some thermodynamic parameters such as isothermal compressibility (κ_T), internal pressure (P_i), solubility parameter (δ) and Pseudo-Gruneisen parameter (Γ).
Isothermal compressibility is an important thermodynamic parameter and has been widely evaluated by many workers [1-3] using several equations of state for pure and mixed liquids; and melts. The knowledge of this parameter may enable one to account for the extent and nature of interactions in solutions. Many researchers [4-8] have employed the isothermal compressibility data for elucidating the intermolecular interactions in amino acids and proteins in aqueous medium.
Internal pressure has been found to be a useful parameter for studying the solute-solvent interactions of bio-molecules in aqueous medium [9-10]. This has been applied in the cases of liquids and liquid mixtures initially by Hildebrand *et al*. [1] and subsequently by several workers [11-15]. Internal pressure turns out to be a measure of the totality of forces including dispersion, repulsion, ionic and dipolar interactions that contribute to the overall cohesion in electrolyte and non-electrolyte aqueous solutions and liquid mixtures.
The Pseudo-Gruneisen parameter has been extensively used by a number of workers [16-18] for investigating the anharmonic properties of liquids. Pseudo-Gruneisen parameter has also been employed to study the thermodynamic behaviour of liquid systems [6].
Present study deals with the study of various thermodynamic parameters of a binary mixture containing Cycloheptane and Methanol.

Experimental
Job's method of continuous variation was adopted to prepare the mixture of different mole fractions of Cycloheptane in the mixture from 0 to 1. The binary mixtures of different compositions were prepared by adding calculated volumes of the components. They were then stirred and kept for a period of 2 hours for stabilization before the measurement of density, ultrasonic velocity at different temperatures. The mixture was kept in tightly closed flask for a sufficiently long time to ensure thermal equilibrium.

A thermostatic water bath was used to maintain a uniform temperature during the measurements. The overall temperature stability was found to within ± 0.01 °C. An ultrasonic interferometer (Mittals, model: F-81) was used for the measurement of sound velocity at a frequency of 2 MHz in the experimental temperature range. The density measurement has been performed by using a pycnometer consist of a small bulb with flat bottom and a graduated stem.

Results and Discussion

The experimental density values of the system under investigation have been least-sqaure fitted to a polynomial of the form,

$$\rho = \sum_{i=0}^{n} \rho_i t^i \text{ (t K)} \quad [1]$$

The coefficients of which along with the standard deviations are listed in Table 1.

The dependence of ultrasonic velocity upon the mole fraction of compounds has been examined by least-square fitting the following polynomial,

$$u = \sum_{i=0}^{n} u_i X^i \quad [2]$$

Where n=2 for binary systems. The results along with the standard deviations are listed in Table 2

Isothermal compressibility of cycloheptane in methanol solution have been computed using the McGowan's [19] expression,

$$\kappa_T = \frac{1.33\times10^{-8}}{\left(6.4\times10^{-4}u^{\frac{3}{2}}\rho\right)^{\frac{3}{2}}} \quad [3]$$

Where u and ρ are the experimental ultrasonic velocity and density data, respectively.

The calculated κ_T values have been listed in Tables 3**.** These values of κ_T have been found to first increase then decrease with increase in mole fraction of cycloheptane. The decrease in κ_T values with increase in concentration seems to be the result of a corresponding decrease in free volume. The κ_T values also show increasing trend with increase in temperature.

Table 1: Least squares fit coefficients of the density equation, $\rho = \rho_o + \rho_1 T + \rho_2 T^2$ as a function of concentration

Cycloheptane + Methanol Solution				
Concentration (X)	**ρ_0 (gcm^{-3})**	**ρ_1 x 10^3 (gcm^{-3} K^{-1})**	**ρ_2 x 10^6 (gcm^{-3} K^{-2})**	**$\sigma_{[\rho]}$ x 10^5**
0.0000	0.8010	-0.0002	0.0000	50.0000
0.0169	0.8012	-0.0003	0.0000	4.7672
0.0544	0.8030	-0.0003	0.0000	22.1495
0.0981	0.8060	-0.0005	0.0000	32.9362
0.1494	0.8086	-0.0006	0.0000	2.4684
0.2107	0.8040	-0.0003	0.0000	36.1515
0.2851	0.8051	-0.0003	0.0000	65.4190
0.3773	0.8086	-0.0004	0.0000	40.2978
0.4946	0.8097	-0.0004	0.0000	99.9607
0.6490	0.8228	-0.0011	0.0000	18.9696
0.8611	0.8283	-0.0012	0.0000	4.5779
1.0000	0.8353	-0.0015	0.0000	0.0000

Table 2: Least squares fit coefficients of the equation, $u = u_o + u_1 m + u_2 m^2$ as a function of temperature

Cycloheptane + Methanol Solution				
Temperature (K)	**u_0**	**u_1**	**u_2**	**$\sigma_{[u]}$**
298.15	1115.50	-694.30	890.88	9.76
303.15	1110.00	-683.50	874.62	14.29
308.15	1083.10	-672.50	859.83	10.68

Table 3: Isothermal compressibility (κ_T x10^{11}, m^{2}N^{-1}) as functions of concentration and temperature

Cycloheptane + Methanol Solution			
Concentration (X)	**Temperature (K)**		
	298.15	**303.15**	**308.15**
0.0000	16.5599	17.2001	17.8969
0.0169	16.8837	17.5350	18.3652
0.0544	17.5421	18.3849	19.3087
0.0981	18.5247	19.3183	20.3398
0.1494	19.4399	20.2419	21.2040
0.2107	20.2026	21.0779	21.9168
0.2851	20.8605	21.7034	22.6497
0.3773	21.2467	22.0651	23.0847
0.4946	20.9084	21.7484	22.7169
0.6490	19.2440	20.0325	20.8882
0.8611	14.6473	15.3586	16.0866
1.0000	10.6310	11.0780	11.5350

This trend of variation may be attributed to the formation of compressible aggregates as a result of increase in temperature as shown in κ_{T1} versus composition plot (Fig.1).

The κ_{T1} values have been further used for evaluating the internal pressure and Pseudo-Gruneisen parameter.

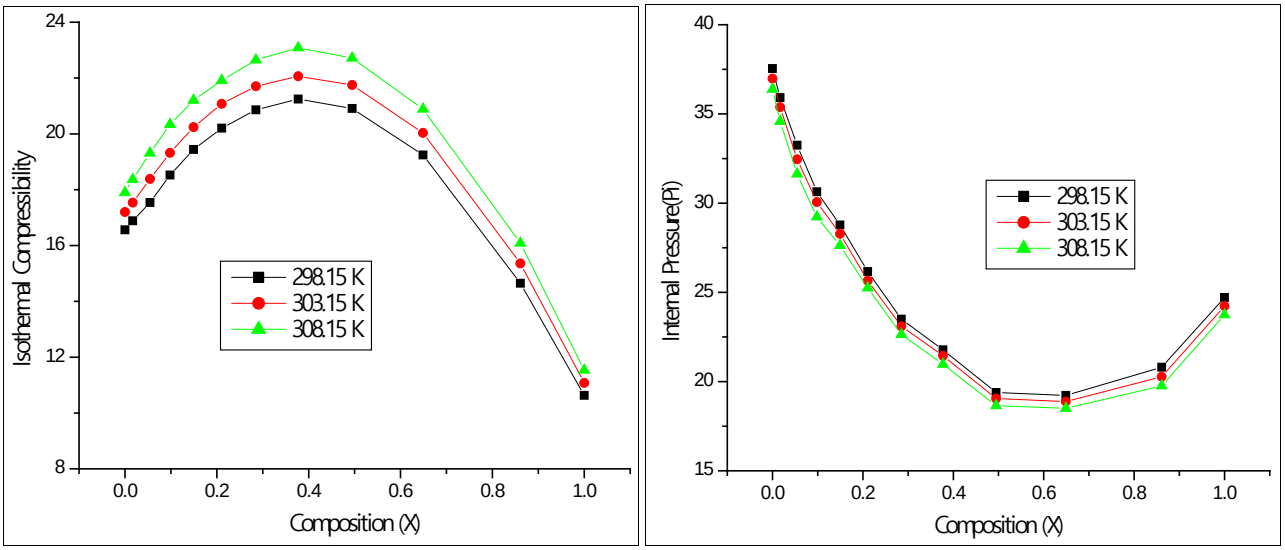

Fig 1: Shown in κ_{T1} versus composition plot

The Internal pressure values of the systems under study have been obtained using the equation (9),

$$P_i = (\alpha_T/\kappa_{T1}) - P \quad [4]$$

The coefficient of thermal expansion, α_T used in evaluating the internal pressure has been calculated from the density data by using the following equation (5):

$$\alpha_T = 1/\rho\ (\partial\rho/\partial T)_P \quad [5]$$

The computed values of P_i are listed in Table 4. The plots of P_i against composition shows decreasing trend with increase in temperature (Fig. 2). An examination of Table 2 reveals that the internal pressure values decrease with increase in mole fraction of cycloheptane. The variation with increase in concentration may be attributed to the overall decrease of cohesive forces in solutions. The decreasing trend of internal pressure may be probable due to a increase in the repulsive forces among the components of the systems with increase in temperature.

Table 4: Internal pressure (P_i x 10^{-8}, Nm^{-2}) as functions of concentration and temperature

Cycloheptane + Methanol Solution			
Concentration (X)	**Temperature (K)**		
	298.15	**303.15**	**308.15**
0.0000	37.5425	36.9816	36.3887
0.0169	35.9152	35.3795	34.5838
0.0544	33.2455	32.4554	31.6353
0.0981	30.6371	30.0593	29.2237
0.1494	28.7764	28.2759	27.6268
0.2107	26.1683	25.6534	25.2468
0.2851	23.4986	23.0964	22.6431
0.3773	21.7823	21.4483	20.9693
0.4946	19.3840	19.0512	18.6487
0.6490	19.2233	18.8810	18.5043
0.8611	20.8021	20.2709	19.7611
1.0000	24.7111	24.2260	23.7417

The Pseudo-Gruneisen parameter, Γ, which happens to be a measure of the degree of molecular/ionic association has been evaluated using the relation (20),

$$\Gamma = \gamma\text{-}1/\alpha_T T \quad [6]$$

in which α and T have their usual meaning. The specific heat ratio, γ has been calculated using the equation (21),

$$\gamma = C_P/C_V = \kappa_{T1}/\kappa_s \quad [7]$$

The values of Pseudo-Gruneisen Parameter have been listed in Table 5. An examination of the table reveals that the values of Γ increase with increase in temperature. This increase may be due to a decrease in the kinetic energy of molecules, which in turn, decrease the thermal motion of molecules and disrupts the molecular association. The Γ values also show a decreasing trend of variation with increase in concentration.

Table 5: Pseudo-Gruneisen parameter (Γ) as functions of concentration and temperature

Cycloheptane + Methanol Solution			
Concentration (X)	**Temperature (K)**		
	298.15	**303.15**	**308.15**
0.0000	-1.3504	-1.3182	-1.2859
0.0169	-1.3839	-1.3511	-1.3178
0.0544	-1.4379	-1.4034	-1.3688
0.0981	-1.4759	-1.4405	-1.4051
0.1494	-1.4959	-1.4601	-1.4245
0.2107	-1.5816	-1.5443	-1.5072
0.2851	-1.7047	-1.6650	-1.6251
0.3773	-1.8052	-1.7631	-1.7213
0.4946	-2.0624	-2.0149	-1.9680
0.6490	-2.2642	-2.2118	-2.1617
0.8611	-2.7659	-2.7034	-2.6444
1.0000	-3.2298	-3.1580	-3.0915

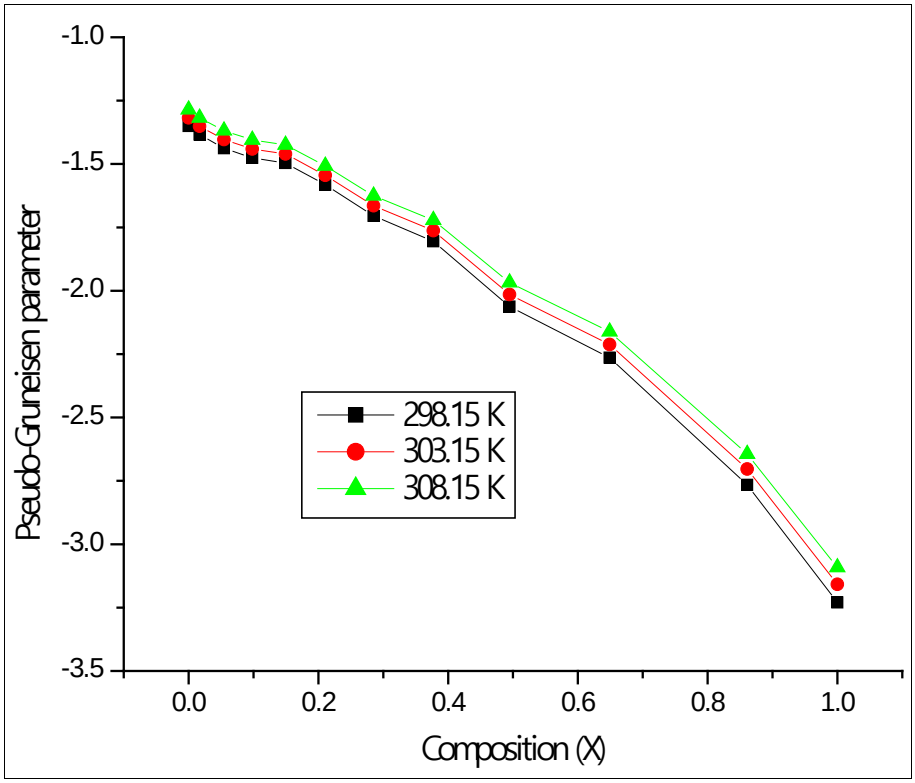

Fig 2: Shows decreasing trend with increase in temperature

Conclusion

The variation in isothermal compressibility of cycloheptane in methanol with concentration and temperature shows a decrease in molecular association. This variation in internal pressure and Pseudo-Gruneisen parameter seems to be due to breaking of clusters of alcohol by the addition of cycloheptane molecule.

References

1. McLure IA, Castillo JMB, Neville JF, Pethrick RA. Ultrasonic velocities, specific volumes, isobaric thermal expansivities, isothermal compressibilities and isochoric thermal pressure coefficients for liquid tetramethylsilane from 224.86 to 273.28 K. Thermochim. Acta. 1994;233:325.
2. Mulero A, Faundez CA, Parra MI, Cuadros F. Theoretical calculations of the isothermal compressibility for simple fluids. Thermochim. Acta. 1999;334:1.
3. Oswal SL, Oswal P, Modi PS, Dave JP, Gardas RL. Acoustic, volumetric, compressibility and refractivity properties and Flory's reduction parameters of some homologous series of alkyl alkanoates from 298.15 to 333.15 K. Thermochim. Acta. 2004;410:1.
4. Hildebrand JH, Scott RL. The solubility of non-electrolytes. 3rd ed. New York: Reinhold; 1964.
5. Suryanarayana CV. The liquid state-A new outlook. J Acoust Soc India; c1977, 5(11).
6. Pandey JD, Pant N, Chaturvedi BR. Evaluation of excess internal-pressure and correlation with interaction in binary-liquid mixtures. Chemica Scripta. 1981;18(5):224-226.
7. Malakondaiah K, Khan VH, Subrahmanyam SV. Isothermal compressibility, internal-pressure and gruneisen-parameter of the systems-benzene+ cyclohexane, cyclohexane+ carbon tetracloride and carbon tetracloride+ benzene on the basis of ultrasonic measurements, the flory theory and the significant structure-theory at 25-degrees-c. Acustica. 1980;45(3):196-200.

8. Nad S, Pal H. Photophysical properties of coumarin-500 (C500): unusual behavior in nonpolar solvents. J Phys Chem A. 2003;107(4):501-507.
9. Chandra P, Singh RK, Soni NK, Priyanka. A Theoretical Study of Internal Pressure of Multicomponent Liquid Mixtures. Int J Innov Eng Technol (IJIET). 2019;13(4):137-145.
10. Hevia F, Alonso V, González JA, Sanz LF, García de La Fuente I, *et al*. Density, speed of sound, refractive index and relative permittivity of methanol, propan-1-ol or pentan-1-ol + aniline liquid mixtures. Application of the Kirkwood-Fröhlich model. J Mol Liquids. 2021;322:114988.
11. Acevedo LI, Pedrosa GC, Katz M. Internal pressure and cohesive energy density for binary non-electrolyte mixtures. J Solution Chem. 1990;19(9):911-921.
12. Shukla RK, Shukla SK, Pandey VK, Awasthi P. Excess internal pressure, excess energy of vaporization and excess pseudoGruneisen parameter of binary, ternary and quaternary liquid mixtures. J Mol Liquids. 2008;137(1-3):104-109.
13. Marczak W. Internal pressure of a thermodynamically ideal mixture and the excess internal pressure. Phys Chem Chem Phys. 2002;4(10):1889-1890.
14. Dey R, Singh AK, Pandey JD. A new theoretical approach for estimating excess internal pressure. J Mol Liquids. 2006;124(1-3):121-123.
15. Nain AK, Chand D, Chandra P, Pandey JD. Excess internal pressures, excess free volumes and excess thermodynamic parameters of some non-aqueous binary mixtures from ultrasonic speed, density and viscosity data. Phys Chem Liquids. 2009;47(2):195-209.
16. Lopes JNC, Rebelo LPN, Jancso G. On the pseudo-Grüneisen parameters of molecular liquids. J Mol Liq. 1992;54:115.
17. Amoros J, Solana JR, Villar E. Temperature, pressure and volume dependence of the Grüneisen parameter of dense gaseous and liquid argon. Mat Chem Phys. 1988;20:255.
18. Sharma BK. Isochoric temperature dependence of the thermodynamic Grüneisen parameter and molecular compressibility of liquid argon. Phys Lett A. 1984;101:405.
19. McGowan JG. Variation of the isothermal compressibilities of liquids with temperature. Nature (London). 1966;210:1255.
20. Shapiro JN, Knopoff L. Pseudo-Grüneisen Parameter for Liquids. Phys Rev B1. 1970;10:3893.
21. Islam MR, Quadri SK. Applicability of floy's statistical theory for the evaluation of excess volume, sound velocity and viscocity. Acoust Lett. 1988;11(12):237.