



Ultrasonic Studies on Binary Liquid Mixtures of Cyclohexane with Carbitols at 308.15 K

S. Bahadur Alisha¹, B. V. Ramesh², K. S. V. Krishna Rao³, M. C. S. Subha⁴, K. Chowdoji Rao⁵

¹Department of Chemistry, S.L.S. Degree College, Pullareddypeta, Andhra Pradesh, India. ²Department of Chemistry, Maris Stella College, Vijayawada, Andhra Pradesh, India. ³Department of Chemistry, Yogivemana University, Vemanapuram, Kadapa, Andhra Pradesh, India. ⁴Department of Chemistry, Sri Krishnadevaraya University, Ananthapuramu, Andhra Pradesh, India. ⁵Department of Polymer Science and Technology, Sri Krishnadevaraya University, Ananthapuramu, Andhra Pradesh, India.

Received 04th March 2017; Revised 11th May 2017; Accepted 25th May 2017

ABSTRACT

Densities and ultrasonic velocities of binary liquid mixtures of cyclohexane with carbitols 2(2-methoxyethoxy) ethanol (methylcarbitol), 2(2-ethoxyethoxy) ethanol (ethylcarbitol), and 2(2-butoxyethoxy) ethanol (butylcarbitol) have been measured at 308.15 K. The observed data have been utilized to calculate various acoustical parameters such as Isentropic compressibility (K_s), Intermolecular free length (L_f), and acoustic impedance (Z). The various excess properties including excess ultrasonic velocity (u^E), excess acoustic impedance (Z^E), excess isentropic compressibility (K_s^E) and excess intermolecular free length (L_s^E) were calculated. The results were discussed in terms of the existence of intermolecular interactions between the components in the liquid mixtures under study.

Key words: Ultrasonic velocity, Cyclohexane, Carbitols, Excess isentropic compressibility, Excess intermolecular free length, Excess acoustic impedance.

1. INTRODUCTION

Ultrasonic investigations of liquid mixtures consisting of polar and non-polar components are of considerable importance in understanding intermolecular interactions between the component molecules and they find applications in several industrial and technological processes [1,2]. Further, such studies as functions of concentration are useful in gaining insight into the structure and bonding of associated molecular complexes and other molecular processes. Further, the variation of ultrasonic velocity and other ultrasonic parameters along with their excess values of binary or ternary liquid mixtures with changing mole fraction of one of the components has been investigated by many researchers [3,4].

Ultrasonic wave propagation affects the physical properties of the medium and hence can furnish information about molecular interactions of the liquid and liquid mixtures. The sign and magnitude of the non-linear deviations from ideal values of velocities and adiabatic compressibilities of liquid mixtures with composition are attributed to the difference in molecular size and strength of interaction between unlike molecules [5,6]. Ultrasonic velocities have been

adequately employed in understanding the nature of molecular interaction in pure liquids [7], binary, and ternary mixtures [8-10]. The method of studying the molecular interaction from the knowledge of variation of thermodynamic parameters and their excess values with composition gives an insight into the molecular process [11,12]. The present paper is part of our research work on thermodynamic properties of liquid-liquid mixtures [13-17]. Cyclohexane is non-polar unassociated inert hydrocarbon possessing a globular structure. It is highly inert toward electrophile or a nucleophile at ordinary temperature. Due to the non-polar nature of cyclohexane and its inertness toward electron donors [18], dispersive type of interactions is expected between it and other components, whereas carbitols are polar and associative in nature. Thus, cyclohexane and its binary mixtures with methyl, ethyl, and butyl carbitols which are having ethereal and hydroxyl oxygen in the same molecule will be interesting to study the molecular interactions. This paper includes density and ultrasonic behavior of binary mixtures of cyclohexane with carbitols over the entire composition range at 308.15 K.

*Corresponding Author:
E-mail: bahaduralisha@gmail.com

2. EXPERIMENTAL

2.1. Materials

Cyclohexane (CH), methylcarbitol (MC), ethylcarbitol (EC), and butylcarbitol (BC) were purchased from E-Merck, Mumbai and used as received.

2.2. Methods

Mixtures were prepared by mixing weighed amounts of the pure liquids adopting the method of closed system using mettler balance with the precision of ±0.1 mg. The ultrasonic sound speeds in pure liquids and their binary mixtures were measured using the single - crystal variayable - path ultrasonic interferometer operating at a frequency of 2 MHz and these were accurate up to ±0.03%. The densities (ρ) of liquids and their mixtures were measured using bicapillary pycnometer having a capillary diameter of 0.85 mm, which was calibrated using double-distilled water. The necessary buoyancy corrections were applied. The density values were reproducible with in ±0.2 Kg/m. Comparing the the purity of compounds the measured values of density and ultrasonic velocity are those reported in literature and was found to be accurate up to ±0.02 kg/m³. The temperature was maintained constant during the period of measurement by a water circulation system from a thermostatically controlled and well-stirred constant temperature water bath, Schott Garate whose temperature was controlled to ±0.02K was used for all measurements. Mixtures were allowed to stand for some time before every measurement so as to avoid air bubbles. The purities of the liquids were checked by comparing the values of densities and ultrasonic velocities with literature. The measurements were made with proper care in an AC room to avoid evaporation loss.

3. RESULTS AND DISCUSSION

From the measured densities (ρ) and ultrasonic velocities (u), the various acoustical parameters such as K_s, Z, and L_f were calculated using the following equations 1-4, respectively, for the binary systems CH+MC, CH+EC, and CH+BC under study.

$$K_s = 1/u^2 \rho \tag{1}$$

$$Z = \rho u \tag{2}$$

$$L_f = K(K_s)^{1/2} \tag{3}$$

Where “K” is Jacobson’s constant [19].

The excess functions Y^E have been calculated using the relation:

$$Y^E = Y_{mix} - (X_1 Y_1 + X_2 Y_2) \tag{4}$$

Where, Y^E is u^E or Z^E or K_s^E or L_f^E and Y denotes u, Z, K_s, and L_f, respectively, X is the mole fraction of BEZ and suffixes 1 and 2 denotes the components

1 and 2 in binary mixtures and are incorporated in Table 1. From table, it is observed that the decrease in u and corresponding increase in L_f with X_{CH} in the systems under study are in accordance with the view proposed by Eyring and Kincaid [20], and observed that u, Z and R_A for the systems CH+MC, CH+EC, and CH+BC decrease nonlinearly with increase in X_{CH} while K_s and L_f exhibit reverse trends, which suggest the presence of molecular interactions between the component molecules [17,10].

The excess functions which are a measure of the deviations from ideal behavior are relatively more sensitive to the inter molecular interactions between unlike molecules, with this view u^E, Z^E, K_s^E, and L_f^E have been calculated using experimental data with the help of equation 4, and these excess functions u^E, Z^E, K_s^E, L_f^E, versus X_{CH} have been shown in Figures 1-4.

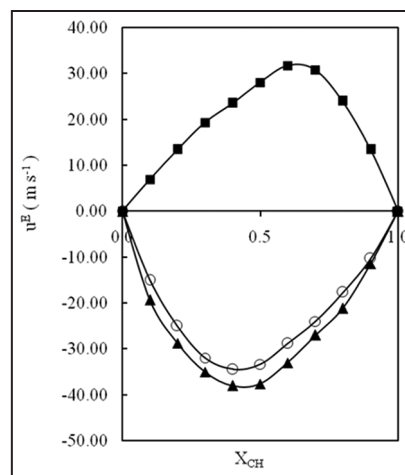


Figure 1: Plots of excess ultrasonic velocity (u^E) versus mole fraction of CH (X_{CH}) at 308.15 K for the binary mixtures of CH with MC (—◆—), EC (—○—), and BC (—▲—).

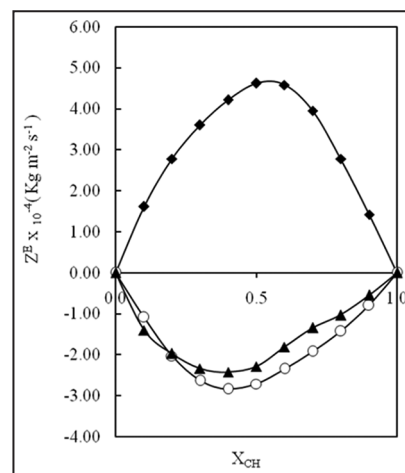


Figure 2: Plots of excess acoustic impedance (Z^E) versus mole fraction of CH (X_{CH}) at 308.15 K for the binary mixtures of CH with MC (—◆—), EC (—○—), and BC (—▲—).

Table 1: Values of density (ρ), ultrasonic velocity (u), excess ultrasonic velocity (u^E), acoustic impedance (Z), excess acoustic impedance (Z^E), isentropic compressibility (K_s), excess isentropic compressibility (K_s^E), intermolecular free length (L_f), excess intermolecular free length (L_f^E), and relative association (R_A) for the binary liquid mixtures of benzene (BEZ) with carbitols at 308.15 K.

Mole fraction of THF (X_{TEA})	$\rho \times 10^{-3}$ ($Kg\ m^{-3}$)	u ($m\ s^{-1}$)	u^E ($m\ s^{-1}$)	$Z \times 10^{-4}$ ($Kg\ m^{-2}\ s^{-1}$)	$Z^E \times 10^{-4}$ ($Kg\ m^{-2}\ s^{-1}$)	$K_s \times 10^{11}$ ($m^2\ N^{-1}$)	$K_s^E \times 10^{11}$ ($m^2\ N^{-1}$)	$L_f \times 10^{12}$ (m)	$L_f^E \times 10^{12}$ (m)	Relative association (R_A)
CH+MC										
0.0000	1.0073	1382.7	0.0000	1.3928	0.0000	51.93	0.0000	4.7724	0.0000	1.0000
0.1002	0.9925	1372.2	6.9148	1.3619	1.6116	53.51	-2.1861	4.8446	-0.7755	0.9878
0.1998	0.9746	1361.4	13.4252	1.3268	2.7748	55.36	-4.0827	4.9277	-1.4336	0.9726
0.2998	0.9543	1349.9	19.3052	1.2882	3.6044	57.51	-5.7001	5.0222	-1.9829	0.9550
0.4001	0.9331	1336.7	23.5374	1.2473	4.2157	59.98	-7.0000	5.1291	-2.4134	0.9368
0.5001	0.9098	1323.8	28.0174	1.2044	4.6183	62.72	-8.0217	5.2450	-2.7494	0.9164
0.5999	0.8833	1310.1	31.6626	1.1572	4.5815	65.96	-8.5367	5.3788	-2.9037	0.8928
0.6997	0.8546	1291.9	30.8079	1.1041	3.9475	70.11	-8.1421	5.5454	-2.7295	0.8678
0.7996	0.8247	1267.7	23.9705	1.0455	2.7749	75.45	-6.5587	5.7528	-2.1489	0.8428
0.9011	0.7941	1239.5	13.4112	0.9843	1.4175	81.97	-3.8640	5.9959	-1.2345	0.8176
1.0000	0.7641	1208.9	0.0000	0.9237	0.0000	89.55	0.0000	6.2672	0.0000	0.7933
CH+EC										
0.0000	0.9748	1345.3	0.0000	1.3114	0.0000	56.68	0.0000	4.9861	0.0000	1.0000
0.1005	0.9582	1316.6	-14.9918	1.2616	-1.0871	60.21	0.2201	5.1388	0.2388	0.9901
0.1996	0.9386	1293.1	-24.9746	1.2137	-2.0314	63.72	0.4743	5.2865	0.4466	0.9756
0.3002	0.9185	1272.4	-31.9527	1.1687	-2.6318	67.25	0.6978	5.4310	0.6025	0.9599
0.4001	0.8978	1256.3	-34.4264	1.1279	-2.8382	70.57	0.7394	5.5636	0.6492	0.9423
0.4997	0.8768	1243.8	-33.3409	1.0906	-2.7112	73.72	0.6156	5.6864	0.6014	0.9233
0.6002	0.8547	1234.6	-28.8327	1.0552	-2.3502	76.76	0.3499	5.8024	0.4736	0.9023
0.7001	0.8327	1225.8	-24.0064	1.0207	-1.9261	79.92	0.2297	5.9208	0.3773	0.8811
0.7995	0.8101	1218.6	-17.6482	0.9872	-1.4262	83.13	0.1658	6.0382	0.2787	0.8589
0.9001	0.7874	1212.2	-10.3264	0.9545	-0.7963	86.43	0.1612	6.1570	0.1775	0.8363
1.0000	0.7641	1208.9	0.0000	0.9237	0.0000	89.55	0.0000	6.2672	0.0000	0.8123
CH+BC										
0.0000	0.9397	1325.3	0.0000	1.2454	0.0000	60.59	0.0000	5.1550	0.0000	1.0000
0.1004	0.9264	1294.3	-19.3134	1.1990	-1.4050	64.44	0.9411	5.3163	0.4956	0.9937
0.1997	0.9121	1273.3	-28.7549	1.1614	-1.9771	67.62	1.2519	5.4461	0.6900	0.9837
0.2998	0.8966	1255.4	-35.0033	1.1256	-2.3358	70.77	1.4974	5.5713	0.8286	0.9715
0.3999	0.8805	1240.8	-37.9516	1.0925	-2.4227	73.77	1.5980	5.6882	0.8839	0.9578
0.5001	0.8635	1229.5	-37.5884	1.0617	-2.2847	76.61	1.5372	5.7967	0.8546	0.9422
0.5997	0.8461	1222.5	-32.9949	1.0344	-1.8125	79.08	1.1258	5.8895	0.6752	0.9250
0.7003	0.8273	1216.8	-26.9851	1.0067	-1.3465	81.64	0.7688	5.9840	0.5008	0.9058
0.7996	0.8074	1211.1	-21.1266	0.9778	-1.0340	84.44	0.6941	6.0858	0.4144	0.8854
0.9002	0.7860	1209.1	-11.4167	0.9504	-0.5470	87.03	0.3666	6.1783	0.2205	0.8624
1.0000	0.7641	1208.9	0.0000	0.9237	0.0000	89.55	0.0000	6.2672	0.0000	0.8384

In general, K_s^E and L_s^E depend on two factors (i) increase in free length, defined by Jacobson [19], due to loss of dipolar association and breaking up hydrogen bonding [21] and differences in size and shapes of the

component molecules and (ii) decrease in free length as a result of dipole dipole interactions lead to hydrogen bonding association [22] complex formation between the component molecules [13]. The first effect decreases

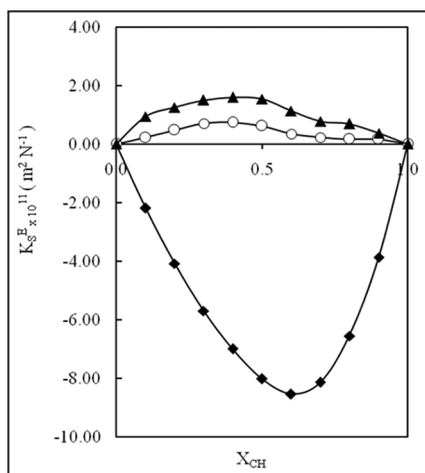


Figure 3: Plots of excess isentropic compressibility (K_s^E) versus mole fraction of CH (X_{CH}) at 308.15 K for the binary mixtures of CH with MC (\blacklozenge), EC (\circ), and BC (\blacktriangle).

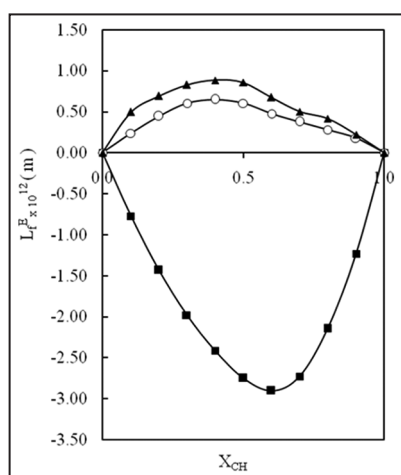


Figure 4: Plots of excess intermolecular free length (L_f^E) vs mole fraction of CH (X_{CH}) at 308.15 K for the binary mixtures of CH with MC (\blacklozenge), EC (\circ), and BC (\blacktriangle).

the ultrasonic speed in the solution as a result of which, its isentropic compressibility increases. The second effect increases the sound speed so that the isentropic compressibility of the solution decreases. The observed K_s^E and L_s^E values are the net result of these two effects. A similar observation was made by Pal and Das [21] from their ultrasonic velocity studies for the binary liquid mixtures. It is observed from the Figures 3 and 4 which show that K_s^E and L_s^E are negative for the system CH+MC and positive CH+EC and CH+BC over the entire composition range. The curves obtained for the systems CH+EC and CH+BC are positive and this reveals that the structural effects are predominant in these mixtures over the effect of complex formation between unlike molecules. Negative K_s^E and L_s^E values may be attributed to the decrease in free length between the molecules due to interstitial accommodation of cyclohexane in the MC. In the systems CH+EC and CH+BC, the loss of dipolar

association in EC and BC leads to increase free lengths. Consequently, sound waves travel smaller distances in the mixtures. This contributes to the positive deviation in K_s^E and L_s^E . The algebraic values of K_s^E and L_s^E are in the following order CH+BC > CH+EC > CH+MC. This order suggests that the strength of interactions decrease with increase in the chain length of alkoxy group of carbitols. This conclusion receives support from the work of Aminabhavi *et al.* [23,24].

It is noticed from the Figures 1 and 2 which show the variation of u^E and Z^E , respectively. u^E and Z^E values are positive for the system CH+MC and negative for the systems CH+EC and CH+BC. The algebraic values of u^E for all the systems under study are in the following order CH+MC > CH+EC > CH+BC. The above order supports our earlier view that the interactions in the binary liquid mixtures CH+EC and CH+BC are weaker than CH+MC mixtures.

From these variations of u^E and Z^E , it is concluded that the specific interactions are present between the unlike molecules which supports our earlier conclusions drawn from the K_s^E and L_f^E . The above trend suggests that the interactions decrease with increase in the chain length of alkoxy group of carbitols. It again supports our view regarding the presence of molecular interactions of these mixtures under study [17].

4. CONCLUSION

Ultrasonic velocity is one of the powerful probes for characterizing the physico-chemical properties of liquid mixtures. Also, the density, ultrasonic velocity and derived excess acoustical parameters provide an evidence of confirmation. It is concluded that the dependence of ultrasonic velocity on composition of the mixtures is satisfactorily explained. The interactions and their order of intensity in the binary liquid mixtures depend on the solvent nature. This may be attributed to the fact that as molecular weights of corbitals increase the ability of hydrogen bond formation will take place due to the increases in the chain length of alkoxy groups in the carbitols which are mainly responsible for molecular interactions with cyclohexane.

5. REFERENCES

1. M. Rastogi, A. Awasthi, M. Gupta, J. P. Shukla, (2002) Ultrasonic investigations of X HO bond complexes, *Indian Journal of Pure and Applied Physics*, **40**: 256.
2. S. Acharya, R. Paikray, G. C. Mohanty, (2003) Ultrasonic study of binary mixtures of DIBK (diisobutylketone) with polar liquids, *Indian Journal of Pure and Applied Physics*, **41**: 855.
3. S. Oswal, A. T. Patel, (1995) Speeds of sound, isentropic compressibilities, and excess volumes of binary mixtures. 2. Mono-n-alkylamines with cyclohexane and benzene, *Journal of Chemical and Engineering Data*, **40**: 194-198.

4. A. Ali, A. Kumar, Abida, (2004) Ultrasonic and volumetric studies of molecular interactions in acetonitrile + 1-alkanol (C6, C8, C10) binary liquid mixtures at different temperatures, *Journal of the Chinese Chemical Society*, **51**: 477.
5. R. Mehra, H. Sanjname, (2000) Acoustical studies in ternary electrolytic mixtures at 25, 30, 35, 40 and 45° C, *Indian Journal of Pure and Applied Physics*, **38**: 760.
6. R. J. Fort, W. R. Moore, (1965) Adiabatic compressibilities of binary liquid mixtures, *Transactions of the Faraday Society*, **61**: 2102-2111.
7. K. V. Lakshmi, D. Suhasini, M. J. Reddy, C. Ravi, K. C. Rao, M. C. S. Subha, (2014) Ultrasonic studies on binary liquid mixtures of tetrahydrofuran with benzenes at 308.15 K, *Indian Journal of Advances in Chemical Science*, **3**: 38-48.
8. P. Nagaraja, C. N. Rao, P. Venkateswarlu, (2016) Excess volumes of binary liquid mixtures of m-xylene with nitrotoluenes, *Indian Journal of Advances in Chemical Science*, **4**: 421-424.
9. J. N. Spencer, E. Jeffrey, C. Robert, (1979) Enthalpies of solution and transfer enthalpies an analysis of the pure base colorimetric method for the determination of hydrogen bond enthalpies, *The Journal of Physical Chemistry*, **83**: 1249.
10. R. J. Rort, W. R. Moore, (1966) Viscosities of binary liquid mixtures, *Transactions of the Faraday Society*, **62**: 1112.
11. A. Murugkar, A. P. Maharolkar, (2014) Ultrasonic study of n-butanol and N-N-dimethyl acetamide binary mixtures, *Indian Journal of Advances in Chemical Science*, **2**: 249-252.
12. R. J. Large Man, W. S. Dundbar, (1945) Relationships between the velocity of sound and other physical properties of liquids, *The Journal of Physical Chemistry*, **49**: 428.
13. S. B. Alisha, N. S. Babu, M. C. S. Subha, (2007) Ultrasonic velocity study of binary liquid mixtures of benzene with cellosolves at 308.15K, *Journal of Pure and Applied Ultrasonics*, **29**: 60-64.
14. M. E. Bai, M. C. S. Subha, G. N. Swamy, K. C. Rao, (2004) Acoustical studies of molecular interactions in binary liquid mixtures of butoxy ethanol with some amines at 308.15 K, *Journal of Pure and Applied Ultrasonics*, **26**: 79.
15. M. E. Bai, K. G. Neerajakshi, K. S. V. Rao, G. N. Swamy, M. C. S. Subha, (2005) Thermodynamic properties of binary mixtures of 2-methoxy ethanol with different amines at 308.15 K, *Journal of the Indian Chemical Society*, **82**: 25.
16. K. V. Lakshmi, D. M. Suhasini, N. J. Reddy, K. R. Kumar, K. C. Rao, M. C. S. Subha, (2014) Density and viscosity studies on binary mixtures of methyl acrylate with benzene and substituted benzenes at 308.15 K, *International Research Journal of Sustainable Science and Engineering*, **2**: 1.
17. S. B. Alisha, K. G. E. Bai, G. Neerajakshi, K. S. V. Rao, M. C. S. Subha, (2002), Ultrasonic velocity study of binary liquid mixtures of cyclohexane with ellosolves at 308.15 K, *Journal of Acoustical Society of India*, **30**: 9-13.
18. S. Thirumaran, K. Jayalakshmi, (2009) Molecular interaction studies on n-alkanols in cyclohexane with DMF at 303K, *Achieves of Applied Science Research*, **1(2)**: 24.
19. B. Jacobson, (1952) Intermolecular frelength in liquid state adiabatic and isothermal compressibility, *Acta Chemica Scandinavica*, **6**: 1485.
20. H. Eyring, J. F. Kincaid, (1938) Free volumes and free angle ratios of molecules in liquids, *Journal of Chemical Physics*, **6**: 620.
21. A. Pal, S. Sharma, G. Dass, (1999), Ultrasonic speeds and volumetric properties of mixtures containing polyethers and 2-methoxyethanol at the temperature 298.15 K, *The Journal of Chemical Thermodynamics*, **31**:273.
22. L. R. O. Storey, (1953) Ultrasonic absorption in mixtures of ethyl alcohol and water, *Proceedings of the Physical Society*, **65B**: 943.
23. T. M. Aminabhavi, I. A. Mrityunjaya, B. H. Shivaputrappa, H. B. Ramachandra, (1993), Densities, viscosities, refractive indices, and speeds of sound for methyl acetoacetate+aliphatic alcohols (C1-C8), *Journal of Chemical and Engineering Data*, **38**: 31.
24. A. Pal, W. Singh, (1997) Speeds of sound and isentropic compressibilities of $\{x\text{CH}_3\text{O}(\text{CH}_2)_2\text{OH}+(1-x)\text{H}(\text{CH}_2)_v(\text{OCH}_2\text{CH}_2)_2\text{OH}\}$ ($v=1, 2, \text{ and } 4$) at the temperature 298.15 K, *The Journal of Chemical Thermodynamics*, **29(6)**: 639-648.

*Bibliographical Sketch



Dr. S. Bahadur Alisha did his B.Sc., from Andhra University, Vizag, India. M.Sc. Chemistry from Agra University, Agra, India. He did his M.Phil. and Ph.D. from Sri Krishnadevaraya University, India. He completed his Ph.D through Faculty Improvement Programme (FIP) of University Grants Commission, India. His major field of research is thermodynamic properties of binary liquid mixtures. He joined as lecturer at Department of Chemistry, S.L.S. Degree College, Pullareddypeta, 516175, India in 1984 and promoted as Reader in Chemistry in the year 2001. He is currently working as Associate Professor in the Department of Chemistry, S.L.S. Degree College, Pullareddypeta-516175, Andhra Pradesh, India. He is Vice-Principal of the college since 2008 onwards.